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DEVELOPMENT OF THE AQUEOUS PROCESSES FOR REMOVING NOx FROM FLUE GASES

Gilford A. Chappell

Esso Research and Engineering Company

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Environmental Protection Technology

Development of the Aqueous Processes for Removing NO_x From Flue Gases

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A screening study was conducted to evaluate the capability of aqueous solutions to scrub NO_x from the flue gases emitted by stationary power plants fired with fossil fuels. The report summarizes the findings of this laboratory program. The experimental program studied the following media for absorption of NO_x from flue gases containing no NO_x: (1) water; (2) metal hydroxides and slurries; (3) ammonia and 2-aminoethanol solutions; (4) acid solutions; (5) salt solutions. In the scrubbing of flue gas containing NO_2 and SO_2, absorption of NO_2-SO_2 by: sulfites; hydroxides; and carbonates was studied. Combined NO_x-SO_x scrubbing seems feasible using any of several hydroxide or carbonate systems provided NO_x (NO) can be efficiently oxidized to NO_2 upstream from the scrubbing unit.

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DEVELOPMENT OF AQUEOUS PROCESSES FOR REMOVING NO_x FROM FLUE GASES

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EPA REVIEW NOTICE

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ABSTRACT

This report summarizes the findings of the laboratory program for "Development of Aqueous Processes for Removing NO_x from Flue Gases" (EPA Contract 68-02-0220). A screening study was conducted to evaluate the capability of aqueous solutions to scrub NO_x from the flue gases emitted by stationary power plants fired with fossil fuels.

The key findings of this program are as follows:

- The addition of NO_2 to flue gas to improve NO_x (mostly NO) absorption does not appear promising. While the presence of NO_2 does improve the absorption of NO, the magnitude of the increase is insufficient to support a viable process.
- Sulfite solutions and slurries are efficient NO_2-SO_2 absorbents. Soluble sulfites (Na_2SO_3) are better NO absorbers than insoluble slurries ($CaSO_3$) because of the higher level of sulfite ion in solution.
- Calcium, magnesium, and zinc hydroxide slurries are effective NO_2-SO_2 absorbers. The sulfite formed when SO_2 is absorbed is necessary for efficient NO_2 scrubbing.
- Limestone ($CaCO_3$) is also a good NO_2-SO_2 absorbent for the same reasons as for $Ca(OH)_2$.
- NO_2 scrubbing is enhanced by removing oxygen from the flue gas or by adding an anti-oxidant such as hydroquinone to the scrubbing solution.
- Sulfide solutions are excellent NO_2 and SO_2 absorbers but do generate a small amount of NO.
- Part of the absorbed SO_2 is oxidized to sulfate.

Combined NO_x-SO_x scrubbing seems feasible using any of several hydroxide or carbonate systems provided NO_x (NO) can be efficiently oxidized to NO_2 upstream from the scrubbing unit.

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Mr. Stanley J. Bunas was the EPA Technical Project Officer during the program.

TABLE OF CONTENTS

Page

ABSTRACT iii

1. INTRODUCTION 1

2. LABORATORY STUDIES 4

    2.1 Apparatus 4

        2.1.1 Flue Gas Blending System 4
        2.1.2 Flue Gas Scrubbers 4

    2.2 Analysis. 8

        2.2.1 Gas Analysis 8
        2.2.2 Solution Analysis. 9

    2.3 Experimental Results. 10

        2.3.1 Absorption of NO_x from Flue Gases Containing No SO_2. 10

            2.3.1.1 NO_x Absorption by Water 10
            2.3.1.2 NO_x Absorption by Metal Hydroxides and Slurries 11
            2.3.1.3 NO_x Absorption bv Ammonia and 2-Aminoethanol Solutions. 14
            2.3.1.4 NO_x Absorption by Acidic Solutions. 15
            2.3.1.5 NO_x Absorption by Salt Solutions. 16
            2.3.1.6 Sulfate Formation in Sulfite Scrubbers. . . 17

        2.3.2 Scrubbing Flue Gas Containing NO_2 and SO_2. 20

            2.3.2.1 NO2-SO_2 Absorption by Sulfites. 20
            2.3.2.2 NO_2-SO_2 Absorption by Hydroxides and Carbonates. 22

        2.3.3 Miscellaneous Scrubbing Experiments. 24

3. CONCLUSIONS AND RECOMMENDATIONS. 28

    3.1 Conclusions 28

    3.2 Recommendations for Future Work 29

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APPENDICES

Page

Appendix A Energy Requirements for Regeneration of Spent Sorbent 30

A.1 Electrochemical Reduction of Sulfate to Sulfite 30

A.2 Thermal Regeneration of MgO from $MgSO_4$ 30

A.3 Thermal Regeneration of MgO from $MgSO_3$ 31

Appendix B Experimental Results - Flue Gas Scrubbing 32

B.1 Emission Data and Run Sheets 35

1. INTRODUCTION

The oxides of nitrogen, NO and NO_2 are essential components in the formation of photochemical smog in addition to being pollutants in their own right. Large fossil fuel fired boilers, such as those found in electric power generating plants, are major sources of these oxides. In such boilers, the nitrogen oxides are formed by the reaction of molecular nitrogen and oxygen in the high temperature combustion zone of the furnace. The immediate product of this reaction is the thermodynamically favored NO. As the combustion gases cool, part of the NO, typically less than 10%, oxidizes to NO_2. The two oxides are generally considered together as NO_x. If the fuels contain organically bound nitrogen, as do coal and oil, part of this nitrogen is also converted to NO during combustion. The composition of different flue gases is shown in Table 1.

TABLE 1

TYPICAL COMPOSITIONS OF FLUE GASES

Component	Volume % Combustion Of		
	Coal(a)	Oil(b)	Gas(c)
N_2	76.2	77.0	72.3
CO_2	14.2	12.0	9.1
H_2O	6.0	8.0	16.8
O_2	3.3	3.0	1.8
SO_2	0.2	0.15	--
NO_x		0.07(d)	
Particulates grams/ft^3	0.5(e)	0.01	--

(a) Calculated for burning with 20% excess air a typical high volatile bituminous coal of the following composition = carbon -70.1%, oxygen -6.6%, hydrogen -4.9%, nitrogen -1.4%, sulfur -3.0%, ash -12.7%, and H_2O -1.3%.

(b) Calculated a typical residual fuel oil of the following composition = 86.5% carbon, 10.3% hydrogen, 2.5% sulfur, 0.7% nitrogen with 20% excess air.

(c) Calculated for burning natural gas with 10% excess air.

(d) This is an average value. Actual values range from 0.01% to 0.15%.

(e) Assumes 90% particulates removal.

In Volume II of the report, "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources" (1-1), Esso Research and Engineering Company assessed the various NO_x control techniques. One promising procedure was aqueous alkaline scrubbing of the flue gas to which NO_2 had been added. Nitric oxide, the chief NO_x constituent, does not itself combine with water or basic solutions. Absorption requires that some of the NO be oxidized to NO_2. A mixture of NO and NO_2 reacts to form a small amount of N_2O_3.

$$NO + NO_2 \rightleftharpoons N_2O_3$$

Sherwood and Pigford (1-2) found the rate of absorption of NO + NO_2 by a 46% NaOH solution to be approximately proportional to the first power of the N_2O_3 concentration, indicating it to be the reacting specie. Mirev et al. (1-3) found that the completeness of the reaction between an NaOH solution and NO/NO_2 mixtures reached a maximum at a 1:1 molar ratio of the oxides.

The N_2O_3 hydrolyzes rapidly in basic solutions to form nitrous acid and nitrite salts.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \xrightarrow{OH^-} 2NO_2^- + 2H_2O$$

Based on the promise of aqueous alkaline scrubbing, a flue gas scrubbing apparatus was constructed and used to screen a large number of potential scrubbing solutions. The original NO_x levels were 350 ppm each of NO and NO_2 with no SO_2 present. The SO_2 was eliminated to simplify the scrubbing chemistry since SO_2 would also be absorbed by the alkaline scrubbers.

The poor results of the early work led to a second phase directed toward NO_2 absorption by aqueous solutions, notably sulfites. This effort presumed the prior oxidation of NO to NO_2 by a suitable technique such as ozone addition or catalysis. In these latter scrubbing studies, SO_2 was usually present in the flue gas and was found to be beneficial for NO_2 absorption. The results from the second phase are quite promising and indicate the possibility of simultaneous NO_2/SO_2 scrubbing.

The objectives of our program were to:

1. Screen various aqueous sorbents for NO_x scrubbing potential using a flue gas containing equimolar NO and NO_2 but no SO_2.
2. Otpimize NO_x absorption in promising systems by varying experimental parameters.
3. Explore effect of SO_2 on NO_x scrubbing.

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1-2 Sherwood, T.K., and Pigford, R.L., "Absorption and Extraction", Chem. Eng. Series, McGraw-Hill, 1952.

1-3 Mirev, D., Balarev, Khr., Boyadzhiev, L., and Lambiev, D., "Absorption of Nitrogen Oxides by Vibrating Layers of NaOH Solutions", Compt. Rend. Acad. Bulgare Sci., 14 : 250-62, 1961.

2. LABORATORY STUDIES

This section of the report describes the laboratory apparatus used to screen the various aqueous solutions and slurries for NO_x scrubbing potential. The experimental results are contained in the latter part of this section.

2.1 Apparatus

The basic scrubbing apparatus consisted of a flue gas blending system and the gas scrubbers. The blending system was capable of producing a wide variety of flue gas compositions by mixing the pure components in different proportions. The flue gas passed through heated lines to the scrubbers where the NO_x and SO_2 were absorbed. The effluent gases were carried by heated lines to the gas analyzers for the determination of the residual NO, NO_2, and SO_2. The different components of the total scrubbing system are described in greater detail below.

2.1.1 Flue Gas Blending System

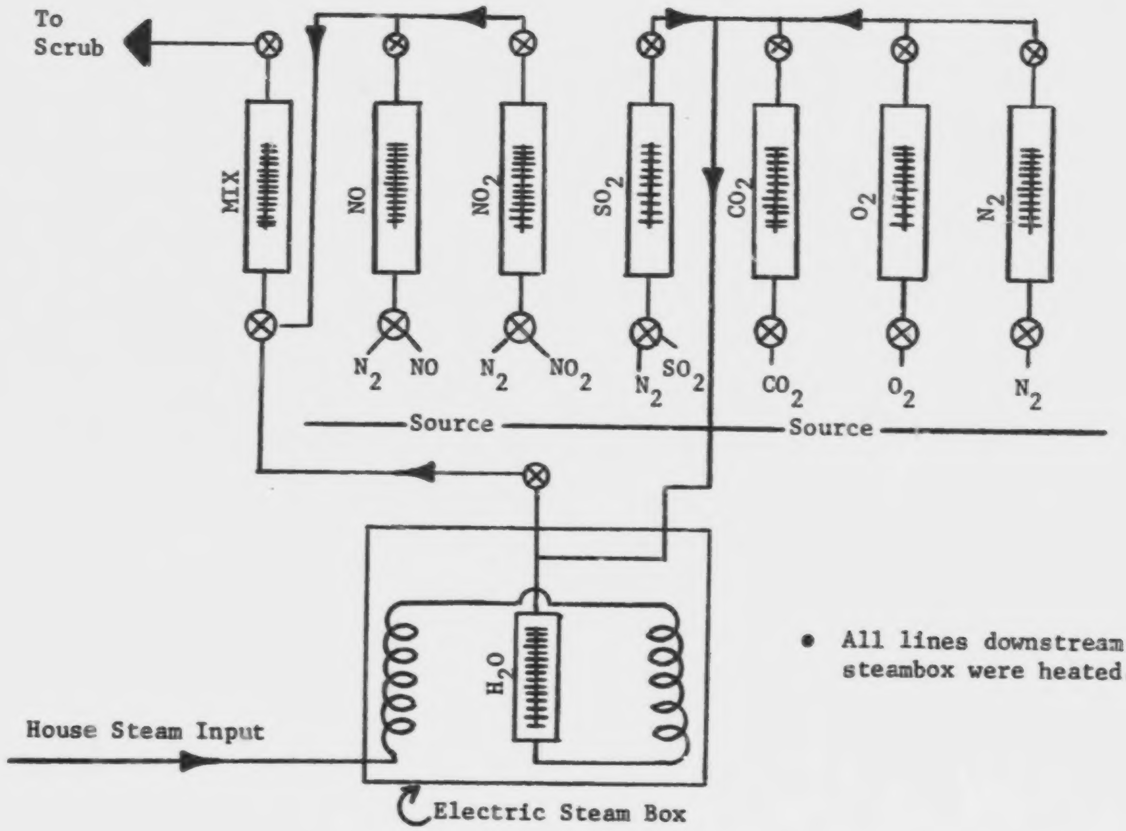
The blending system was designed to produce a heated flue gas from the various components contained in cylinders. The flue gas contaminants SO_2, NO_2, and NO were each contained in a separate high pressure gas cylinder at 5 mole % (50,000 ppm) with nitrogen making up the balance. Other cylinders contained pure oxygen, pure CO_2 and pure nitrogen. Each gas was delivered through 0.25 inch O.D. stainless steel tubing to a calibrated rotameter for flow measurement prior to mixing. Wet steam, which was available in the laboratory, was dried by passing through heated aluminum coils. The dry, hot steam also passed through a calibrated rotameter before mixing with the other components. Figure 2-1 shows a schematic of the gas blending system. The order of mixing was important for minimizing gas phase reactions between NO_2 and SO_2.

$$NO_2 + SO_2 \longrightarrow NO + SO_3$$

After passing through their respective rotameters, N_2, CO_2, O_2, and SO_2 fed into a common line which passed through the heated steam box where steam was added to the mixture. At this point the dewpoint of the gas was about 115°F and the lines were maintained at approximately 200°F. After blending with NO and NO_2, the entire mixture passed through a heated rotameter to determine the total flow rate. The synthetic flue gas was delivered through heated lines to the gas scrubbers. The composition of a typical blend was 350 ppm NO, 350 ppm NO_2, 2400 ppm SO_2, 3 mole % O_2, 12 mole % CO_2, 10 mole % steam, and N_2 as the balance. The flue gas blending system functioned satisfactorily.

FIGURE 2-1

GAS BLENDING SYSTEM


To Scrub
MIX
NO
NO_2
SO_2
CO_2
O_2
N_2
N_2 NO
N_2 NO_2
N_2 SO_2
CO_2
O_2
N_2
Source
Source
H_2O
House Steam Input
Electric Steam Box

- All lines downstream of the steambox were heated.

A recurring annoyance, however, was the destruction of the viton 'O' rings in the rotameters by NO_2. This corrosive gas should not contact anything organic for long time periods except possibly teflon. The degradation products from the viton tended to foul the rotameters, which necessitated periodic cleaning. Fortunately, this did not occur often.

The heated steel lines initially underwent a conditioning process bv the flue gas. The composition of gas exiting from the system varied for 10-20 minutes before stabilizing. If the system was not used for several days, the lines required reconditioning.

No gas phase reactions were observed. Nitric oxide (NO) was not oxidized to NO_2 in the lines and NO_2 did not react with SO_2 at these low concentrations.

2.1.2 Flue Gas Scrubbers

The gas scrubber was a two-liter round-bottom glass flask containing one liter of scrubbing solution or slurry. A teflon-coated magnetic stirring bar agitated the solution. The scrubber temperature was maintained by an electric heating mantle which was controlled by a thermocouple immersed in the solution. The thermocouple was clad with stainless steel. The temperatures of the scrubbing solution, the heated lines, and the steam box were continuously recorded by a 24 point temperature recorder.

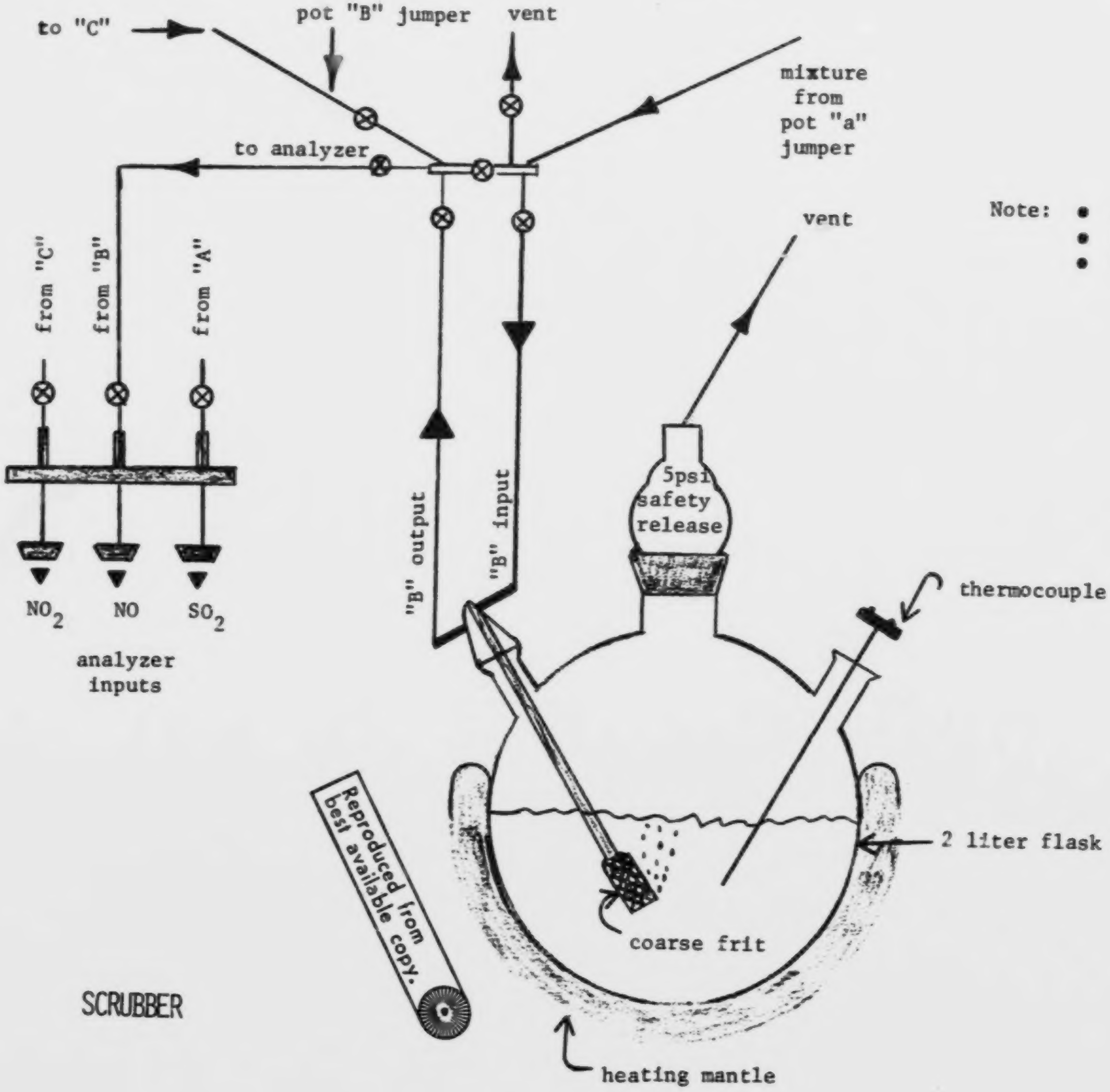
The hot flue gas was introduced into the absorbing solution through a porous glass frit located approximately four inches below the surface.

The temperature of the scrubber was maintained at approximately 125°F for most runs. This is the approximate adiabatic humidification temperature of an actual flue gas.

Figure 2-2 contains a schematic of the scrubber portion of the system. Three scrubbing units were available and could be run in series or parallel. This flexibility allowed one significant advantage in that we could quickly start a second run after finishing the first by simply turning several valves and directing the flue gas to bypass the first scrubber and to enter the second. Thus, the second scrubber could be set up and heated to the operating temperature while the first scrubber was running.

The gas exiting from the scrubber was carried by heated lines to the gas analyzers which measured the NO, NO_2, and SO_2 levels.

FIGURE 2-2


to "C"
pot "B" jumper
vent
mixture from pot "a" jumper
to analyzer
from "C"
from "B"
from "A"
NO_2
NO
SO_2
analyzer inputs
"B" output
"B" input
vent
5psi safety release
thermocouple
2 liter flask
coarse frit
heating mantle

Note:
- all lines are stainless steel,
- all lines heated,
- all connections either ground glass or swagelok

SCRUBBER

Reproduced from best available copy.

2.2 Analysis

2.2.1 Gas Analysis

The heated line carrying the scrubber effluent entered a junction from which three lines exited. These lines transferred the hot gas to the analyzers for measurements of the NO, NO_2, and SO_2 levels.

The SO_2 and NO_2 were analyzed independently by two DuPont 400 spectrophotometers. These were double-beam instruments containing analyzer cells maintained at 212°F. The flue gas passed through the cells continuously. The two analyzers were totally separate except that they shared the same light source; the two gas cells were oriented at 90° to each other. Each analyzer contained a set of filters to isolate the pertinent spectral line. Each unit also had a calibration filter which was equivalent to a fixed ppm level of gas at a fixed temperature and total pressure. The filter was normally outside the light path but could be positioned in the beam to check the response of the instrument. The signals from the NO_2 and SO_2 analyzers were recorded continuously by strip chart recorders. The two DuPont instruments were rugged and reliable and no difficulties were encountered.

The NO analysis involved considerable problems. Initially, a Whitaker "NO_x Box" measured total NO_x (NO + NO_2) and was insensitive to water vapor. However, the flue gas had to be cooled below its dewpoint before analysis in order to keep water droplets from forming inside the instrument. Unfortunately, the water trap removed part of the NO_x from a flue gas containing equal parts NO and NO_2. This occurred by the hydrolysis of N_2O_3 within the trap to yield nitrous acid and nitrate ion. The N_2O_3 forms in the vapor phase from NO and NO_2.

$$NO_{(g)} + NO_{2(g)} \rightleftharpoons N_2O_{3(g)}$$

$$N_2O_{3(g)} + H_2O(1) \rightleftharpoons 2HNO_2 \text{ (in solution)}$$

Eventually, the trap would equilibrate with the gas stream and NO_x fluctuations would cease. This problem caused a significant lag in the response of the instrument to changes in the NO_x levels. If the primary NO_x constituent is NO, this problem does not occur.

Following the initial attempts with the Whitaker NO_x Analyzer, a Beckman NDIR (Non-Dispersive Infra-Red) was used for NO measurements because of its better signal stability and because it read NO directly, not total NO_x. However, all of the water had to be removed from the gas because the instrument read the moisture as NO.

In order to eliminate the $NO-NO_2-H_2O$ interaction in the water trap, the NO_2 had to be removed before the trap. After trying several approaches, a saturated solution of sodium sulfite at room temperature was finally adopted for use as the NO_2 absorber because of its capacity to remove all traces of NO_2. Part of the NO was also removed by the Na_2SO_3 trap, but the fraction of the NO absorbed depended on the amount of NO_2 in the gas stream. The sulfite trap was calibrated with known gas mixtures so that the NO level before the sulfite trap could be calculated from the NDIR reading, the NO_2 reading, and the calibration chart. In the final arrangement for NO analysis, the flue gas passed through the Na_2SO_3 solution, then entered a cold trap chilled with dry ice and methanol. The dry gas was warmed to room temperature before entering the NDIR. The cold trap was packed with glass beads to increase surface area and to reduce the dead volume.

The sulfite trap also removed all SO_2 from the gas stream. Had this not occurred, the SO_2 would have condensed in the water trap.

The final configuration of the gas analysis section proved to be reliable and stable and was used for the majority of the experiments.

2.2.2 Solution Analysis

As the nitrogen oxides are absorbed by the alkaline scrubbing solution, nitrite and nitrate ions are produced.

$$N_2O_{3(g)} + H_2O(1) \longrightarrow 2HNO_2(aq)$$

$$HNO_2 + OH^- \longrightarrow H_2O + NO_2^-$$

$$2NO_{2(g)} + H_2O\ (1) \longrightarrow HNO_{2(aq)} + HNO_{3(aq)}$$

$$HNO_3 + OH^- \longrightarrow H_2O + NO_3^-$$

At first, an Orion Specific Ion Electrode was used for nitrate ion measurements. The nitrite level was determined by oxidizing the NO_2^- to NO_3^- with hydrogen peroxide followed by a total nitrate measurement; the initial nitrate reading was then subtracted from the total nitrate. While this procedure worked well with dilute solutions, it proved somewhat cumbersome. With concentrated salt solutions, interference becomes a problem so a spectrophotometric procedure developed by Wetters and Uglum (2-1) was used.

Simultaneous determinations of nitrite and nitrate were achieved by measuring the light absorption of the sample at two different wavelengths in the ultraviolet region. Nitrite absorbs at 355 nm and 302 nm with molar absorptivities of 23.3 and 9.12 respectively, whereas nitrate absorbs only at 302 nm with a molar absorptivity of 7.24. The absorbance due to nitrate in a sample can be calculated by dividing the nitrite absorbance at 355 nm by 2.5 and subtracting the quotient from the total absorbance at 302 nm. We used cells with a path length of four centimeters to measure nitrate and nitrite levels down to 1×10^{-4} molar. The procedure was rapid and reliable. However, at high pH, CO_2 produces carbonate ion which interferes with the spectrophotometric measurement. Also, nitrite ion converts to nitrous acid at a pH less than 5 and this species interferes with the determination. Most measurements were made in a pH range of 7.5 to 9.5.

Sulfate ion also formed in the scrubber and derived from the oxidation of sulfite ion by oxygen and NO_x. In some experiments, the sulfite was added to the scrubber as a salt (e.g., Na_2SO_3), whereas in other runs the species was produced by the absorption SO_2 from the flue gas by the scrubbing solution. Once formed, the sulfate level was determined by the standard gravimetric procedure which involved acidification with HCl followed by boiling and then precipitation with $BaCl_2$ solution. This is one of the most accurate of analytical procedures.

2.3 Experimental Results

The first part of the program used a flue gas containing equal parts NO and NO_2 but no SO_2. The absence of SO_2 simplified data interpretation. In addition, the NO_x scrubber in an actual system might be located downstream from the SO_2 level in the gas entering the NO_x unit.

The second part of the program was concerned with NO_x and SO_2 absorption by solutions and slurries. In particular, NO_2 scrubbing by sulfites was investigated. In these experiments the flue gas contained SO_2.

The details of each run are recorded in Appendix B.

2.3.1 Absorption of NO_x From SO_2 Free Flue Gas

2.3.1.1 NO_x Absorption by Water

The first series of runs used water to scrub a flue gas containing 3% oxygen, 8-10% steam, 12% CO_2, approximately 350 ppm each of NO and NO_2, and nitrogen as the balance. The flow rate was 3200 cc/min at room temperature (75°F) and pressure. Table 2 contains some of the results.

TABLE 2

NO_x SCRUBBING WITH WATER

Exp. #	Input (ppm)		% Absorption*		Solution	Run Time
	NO	NO2	NO	NO_2	Temp. (°F)	(min)
11-10-71	400	390	-5**	18	125	220
11-16-71	175	400	-9**	23	123	220
11-17-71	360	380	1	23	129	250
11-18-71	305	350	-6**	20	126	240

---

* % of the input concentration being absorbed at the end of the run.

** Negative absorption signifies net % generation.

Nitric oxide was absorbed during the early part of the runs, but as the level of nitrous and nitric acid increased, NO was generated by the hydrolysis of NO_2.

$$3NO_2 + H_2O \longrightarrow NO + 2HNO_3$$

During experiment #11-10-71, an average of 45 ppm of NO_x was absorbed for 215 minutes. The total dissolved NO_x should have been 0.9×10^{-3} molar. Solution analysis yielded 0.9×10^{-3} molar nitrate and 0.2×10^{-3} molar nitrite which totaled 1.1×10^{-3} molar. This constitutes a reasonably good NO_x mass balance. In addition, the agreement in scrubbing efficiency among the runs listed in Table 2 shows good experimental reproducibility.

2.3.1.2 NO_x Absorption by Metal Hydroxide Solutions and Slurries

The hydroxides of sodium, calcium, magnesium, and zinc were investigated for their scrubbing potentials. Both slurries and solutions were used and gave somewhat different results. Table 3 contains a summary of the data which may be found in its entirety in the Appendix. The total gas flow rate was 3200 cc/min in all experiments. The two NaOH runs listed with the Ca and Mg runs used solutions with the same initial pH as the saturated solution of the corresponding metal hydroxide. The scrubbing efficiency varied somewhat during a run so the values in Table 3 are approximate.

TABLE 3

NO_x SCRUBBING WITH METAL HYDROXIDES

Exp. #	Absorbent	Initial pH	Input (ppm)		% Absorption		Solution Temp. (°F)	Run Time (min)
			NO	NO2	NO	NO2		
11-19-71	5N NaOH	14	350	400	20	18	126	180
12-5-71	5N NaOH	14	274	320	35	34	112	60
1-19-72	50 Wt. % NaOH	14	345	330	28	23	120	30
1-27-72	14.8 molal (45 Wt %) NaOH	14	333	360	47*	28	80	80
2-8-72	$Ca(OH)_2$ Slurry**	11.5	353	365	20	21	124	130
12-20-71	$Ca(OH)_2$ Sat. Soln.	11.5	390	380	8	29	121	300
12-7-71	NaOH	11.5	311	360	10	29	120	130
2-9-72	$Mg(OH)_2$ Slurry	8.9	330	350	6	23	125	60
12-13-71	$Mg(OH)_2$ Sat. Soln.	8.9	377	360	7	22	122	80
12-17-71	NaOH	8.9	404	370	6	24	120	90
2-9-72	ZnO Slurry	7.5	353	370	7	16	121	130
12-15-71	ZnO Sat. Soln.	7.5	400	400	8	29	119	90

---

* This value decreased to 28% as the solution temperature increased to 140°F.

** The porous glass frit plugged with $CaCO_3$ early in the run and had to be replaced with an open tube.

In most of the runs, the NO_2 absorption was only slightly improved over pure water; however, the NO absorption was significantly better in several experiments. A qualitative temperature effect was observed in the first four NaOH runs listed in the Table. As the temperature of the scrubbing solution decreased, the scrubbing efficiency increased.

The data from the saturated solutions of $Mg(OH)_2$ and $Ca(OH)_2$ agree with the data from the corresponding NaOH solutions which implies a pH effect. Thus, the $Ca(OH)_2$ system was more alkaline than the $Mg(OH)_2$ system and absorbed more NO_x. Increasing the pH to 14 (5N NaOH) from 11.5 did not improve the absorption efficiency at the same temperature which indicates that the influence of pH is not simple. The ZnO $[Zn(OH)_2]$ slurry absorbed only 16% of the NO_2 whereas the solution absorbed 29%. This seems unusual and no explanation is proposed.

The NO_x mass balance between solution and gas phase was determined at the end of several runs. In general the balance is satisfactory as shown in Table 4. The one exception is exp. #12-17-71 where the solution analysis is much greater than the gas analysis. This is probably due to dissolved carbonate from the CO_2 in the flue gas.

TABLE 4

NO_x MATERIAL BALANCE

		Time	NO_x Absorption (ppm)		Solution Anal		Total Dissolved NO_x Calculated From	
Exp. #	Absorbent	(min)	ΔNO	ΔNO_2	NO_3^-	NO_2^-	Gas Anal.	Sol'n Anal
12-17-71	NaOH (pH = 8.9)	70	30	95	0.3*	1.3*	1.1*	1.6*
12-20-71	$Ca(OH)_2$ sol'n	300	32	125	0.4	4.6	5.9	5.0
12-13-71	$Mg(OH)_2$ sol'n	80	25	100	0	0.9	1.2	0.9
12-15-71	ZnO sol'n	90	25	115	0.3	1.4	1.6	1.7

---

* Concentration unit is millimoles per liter.

Although the overall balance is reasonable, the ratio of nitrite to nitrate in solution is significantly higher than expected, assuming that only simple hydrolysis occurs.

$$3NO_2 + H_2O \longrightarrow NO + 2HNO_3 \text{ (source of nitrate)}$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2 \text{ (source of nitrite)}$$

The data in Tables 3 and 4 indicate that the hydroxide scrubbers are not good NO_x absorbers in the absence of SO_2 and NO_2 recycle is not attractive under these conditions.

2.3.1.3 NO_x Absorption by Ammonia and 2-Aminoethanol Solutions

The best NO removal observed occurred with a 28 Wt. % NH_4OH scrubbing solution which removed 74% of the NO and 80% of the NO_2. Table 5 contains these results in addition to scrubbing data from a similar system, 2-aminoethanol.

TABLE 5

NO_x SCRUBBING WITH AMINES

		Input (ppm)		% Absorption		Solution	Run Time
Exp #	Absorbent	NO	NO_2	NO	NO_2	Temp. (°F)	(min)
1-26-72	NH_4OH (28 Wt %)	330	355	74	80	70	40
2-3-72	2AE*	340	320	40	91	128	95
2-4-72	50% 2AE**	340	330	48	88	127	120
2-4-72	25% 2AE	347	350	48	86	127	110
3-8-72	25% 2AE	360	360	47	89	126	480

---

* 2AE is 2-aminoethanol.

** 50% by volume 2AE and 50% water.

The vapor pressure of NH_3 above the NH_4OH scrubber dicated operation at room temperature. A water scrubber (one liter of H_2O at 70°F) was placed downstream from the NH_4OH scrubber to trap NH_3 vapors for continued scrubbing. Thus, the data in the table result from two scrubbers in series. When the water scrubber was by-passed, the % absorption changed to 54% for NO and 58% for the NO_2. A flask containing dilute H_2SO_4 was placed downstream from water scrubber to protect the analyzers from ammonia vapor. The H_2SO_4 trap was saturated with NO_x before putting the NH_4OH scrubber on line. The interdependence of NO-NO_2 absorption was shown by varying the input levels of each specie. Halving the NO_2 input dropped the NO absorption from 74% to 49%. On the other hand, reducing the NO input to zero dropped the NO_2 absorption from 80% to 51%. The problems associated with the high NH_3 vapor pressure led to considering a higher boiling amine, 2-aminoethanol, for scrubbing.

The vapor pressure of 2-aminoethanol (2AE) is much lower than that of 28 Wt. % NH_4OH. The pure amine has a vapor pressure of 7 Torr at 150°F whereas the NH_3 partial pressure over the ammonia solution is 570 Torr at 70°F. The use of 2AE in the scrubber did not eliminate the need for a dilute H_2SO_4 trap. The small amount of amine vapor emanating from the NO_x absorber had to be removed before the gas stream entered the analyzers. The mist which formed above the scrubbing fluid when NO_2 was present in the flue gas, was removed from the effluent by the H_2SO_4 trap. Before recording data, this trap was saturated with NO_x. As Table 5 shows, the 2AE solutions were excellent NO_x scrubbers but did not remove as much NO as did the ammonia solution. The 2AE was observed to heat up when CO_2 was present in the flue gas indicating that CO_2 is reacting with the solution. This is to be expected since this type of compound is used commercially for scrubbing CO_2 from gas streams. The color of the 2AE solutions changed from colorless to orange as the runs progressed. An attempt to determine the exact nature of the reaction proved inconclusive. A variety of products may result when a primary amine reacts with N_2O_3 ($NO + NO_2$). These include molecular nitrogen (N_2), alkyl ammonium nitrites and nitrates, and alkyl nitrites and nitrates. Secondary amines form dialkylammonium nitrites and dialkyl N-nitroso compounds which are colored. These reactions are essentially irreversible.

2.3.1.4 NO_x Absorption by Acidic Solutions

In order to compare the NO_x absorption potential of acidic solutions with alkaline baths several runs were made with sulfuric acid and glacial acetic acid. The results were not particularly impressive as indicated by Table 6.

TABLE 6

NO_x ABSORPTION BY ACIDS

Exp. #	Absorbent	Input (ppm) NO	Input (ppm) NO_2	% Absorption NO	% Absorption NO_2	Solution Temp. (°F)	Run Time (min)
12-3-71	H_2SO_4 (79 Wt. %)	350	350	1.	14.	202	120
4-25-72	H_2SO_4 (30 Wt. %)	350	300	0	20.	120	110
1-19-72	Glacial Acetic Acid	335	370	0	80	120	20

Approximately 18 ppm of SO_2 was generated during run # 4-25-72. The SO_2 analyzer was not turned on during run # 12-3-71 so SO_2 may also have been produced in that experiment. Sulfuric acid is a poor NO_x absorber whereas acetic acid removes most of the NO_2 but no NO.

2.3.1.5 NO_x Absorption by Salt Solutions

A number of aqueous salt solutions have been screened for NO_x scrubbing potential and some of these appear very promising. Table 7 summarizes the experimental data.

TABLE 7

NO_x ABSORPTION BY SALT SOLUTIONS

Exp. #	Absorbent	Input (ppm) NO	Input (ppm) NO_2	% Absorption NO	% Absorption NO_2	Solution Temp. (°F)	Run Time (min)
12-5-71	4.1m $(NH_4)_2\ SO_3$*	328	350	23	100	112	150
12-21-71	5N NaOH Sat'd with Na_2SO_3	357	355	12	100	129	25
12-21-71	same as above	380	330	27	100	70-85	140
1-3-72	Sat'd Na_2SO_3	375	350	21	100	122	60
1-10-72	$\left\{\begin{matrix}\text{3.6m } NH_4HSO_3\text{**} \\ \text{1.9m } NH_4HSO_4\end{matrix}\right\}$	360	330	24	100	125	90
1-17-72	6M NaOAc	340	360	18	25	119	100
1-18-72	8.4m NH_4Cl	330	350	27	49	123	80
1-24-72	8.4m NH_4OAc	362	360	31	39	123	160
1-28-72	2.3m Na_2SO_3	355	500	18	100	122	60
2-15-72	2.5m Na_2SO_3	358	350	16	100	127	60
2-10-72	1.0m Ammonium Citrate	358	350	25	26	126	90
3-3-72	1.0m Na_2SO_3	355	400	15	100	124	40
3-7-72	$CaSO_3$ Slurry	390	380	33	60	125	40

---

* 4.1m $(NH_4)_2SO_3$ means 4.1 molal $(NH_4)_2SO_3$.

** Copius amounts of SO_2 were generated during solution preparation and during scrubbing run. The pH at the start of the run was 2.4.

Not included in the table is scrubbing run # 1-26-72 which involved passing flue gas through a 2.3 molal solution of Na_2S. Despite some experimental difficulties, the results show 100% absorption of NO_2 and minor absorption of NO from a flue gas containing approximately 350 ppm of each.

The data in Table 7 has one, very clear, message; sulfite ion is an excellent NO_2 absorbent but a poor NO absorbent. The agreement between several Na_2SO_3 runs again demonstrates the stability and reproducibility of our procedures. Runs # 1-3-72, 1-28-72, and 2-15-72 all show 100% absorption of NO_2 and 21%, 18%, and 16% reduction of NO, respectively. Also, run # 1-10-72 shows that low pH and high sulfate levels do not inhibit the absorption of NO_2 by sulfite or bisulfite solutions. The absorption of NO by the $(NH_4)_2SO_3$ solution (run # 12-5-71) dropped to zero when NO_2 was eliminated from the flue gas. In addition, a NO_x material balance was made for the $(NH_4)_2SO_3$ run and after 140 minutes on line, the gas analysis indicated a loss of 7.5 millimoles of NO_x (6.3 NO_2 and 1.2 NO) whereas the solution analysis showed 5.8 millimoles of dissolved NO_x (5.2 NO_3^- and 0.6 NO_2^-). A similar balance determined at the end of run # 1-28-72 (2.3m Na_2SO_3) showed a loss of 4.4 millimoles of NO_x (3.9 NO_2 and 0.5 NO) from the flue gas and 2.4 millimoles of NO_x (2.0 NO_3^- and 0.4 NO_2^-) dissolved in the scrubber. The reason for the imbalance is unclear. Another balance was measured at the end of run # 2-15-72. In this case, the gas analysis indicated a loss of 3.2 millimoles of NO_x (2.7 NO_2 and 0.5 NO) while solution analysis gave 5.3 millimoles of dissolved NO_x (4.2 NO_3^- and 1.1 NO_2^-).

2.3.1.6 Sulfate Formation in Sulfite Scrubbers

When flue gas containing oxidants such as NO_x and O_2 is bubbled through a sulfite containing scrubber, some sulfate is formed which constitutes a problem if solution regeneration is comtemplated. In order to ascertain the magnitude of the problem, several runs were made with saturated sodium sulfite solutions. The flue gas did not contain SO_2 but did have 350 ppm each of NO and NO_2, 3% O_2, 8% H_2O, 12% CO_2, and the balance was nitrogen. Runs were made with and without O_2 and NO. In addition, hydroquinone (HQ) was used in some scrubbers to reduce oxidation. Table 8 contains the results.

TABLE 8

SULFATE FORMATION IN SATURATED Na_2SO_3 SCRUBBERS

Flue Gas →	Complete	Complete	Without NO_x	Without O_2	Without O_2	Without NO_x
Scrubber →	no HQ	with HQ	with HQ	with HQ	no HQ	no HQ
Initial $SO_4^=$ (wt. %)	1.28	0.33	0.22	0.31	0.46	0.10
Final $SO_4^=$ (wt. %) (60 min on line)	1.51	0.61*	0.23	0.37	0.58	0.40
Δ_{60}	0.23	0.28	0.01	0.06	0.12	0.30
millimoles $SO_4^=$ formed	29.	36.	1.3	7.6	15.	39.

---

* Run lasted for 70 minutes.

The scrubbing solution consisted of one liter of liquid whose specific gravity was 1.22. All of the NO_2 was absorbed plus 60 ppm of the NO with gave a total NO_x absorption of 410 ppm. The solutions absorbed 3.2 millimoles of NO_x per hour while being exposed to 234 millimoles of oxygen per hour. The presence of hydroquinone did reduce sulfate formation except in the case of the "complete" flue gas; however, these two runs may be suspect due to the unusually high initial and final sulfate levels. The data suggest that oxygen is involved in the oxidation of sulfite to sulfate.

The effect of initial pH upon the sulfate formation was investigated in 1.0 molal Na_2SO_3 scrubbers. The flue gas did not contain SO_2 but did have 380 ppm NO_2 and 370 ppm NO. All of the NO_2 and 60 ppm of the NO were absorbed by the solutions. The initial pH was raised by adding a small amount of concentrated NaOH and was lowered with hydrochloric acids. The pH changed rapidly upon introducing flue gas into the solution. These runs lasted for 50 minutes and Table 9 contains the results.

TABLE 9

EFFECT OF pH ON SULFATE FORMATION

Initial pH →	7.7	9.6	12.5
Wt. % $SO_4^=$ (t = o)	0.51	0.73	0.33
Wt. % $SO_4^=$ (t = 25 min)	0.74(7.6)	0.86(7.9)	0.64(8.0)
Wt. % $SO_4^=$ (t = 50 min)	0.97(7.6)	0.97(8.0)	0.90(8.1)
Δ_{50}	0.46	0.24	0.57

The numbers in parentheses are the pH's at the end of the specified time. No trend is apparent, but as before, more sulfate is formed than NO_x absorbed.

In other runs, an aqueous slurry containing 8 grams of $CaSO_3$ per liter was used to scrub NO_x and to generate sulfate data. Several different initial pH's were employed with the results shown in Table 10.

TABLE 10

NO_x SCRUBBING BY $CaSO_3$

Initial pH	Input NO	Input NO_2	Input SO_2	Δ NO (ppm)	Δ NO_2 (ppm)	Δ SO_2 (ppm)
7.2	380 ppm	380	0	132	250	--
8.0	390	370	0	132	220	--
12	390	370	0	125→187→125	370→150	--
7.6	0	340	500	--	220	500→440

The first three runs, which did not involve SO_2, lasted for 50 minutes each. The best NO_x absorption occurred in the most basic slurry. The pH was raised to 12 by the addition of a small amount of concentrated NaOH solution. In this run, the NO absorption increased linearly with time over a 40 minute period. After 40 minutes, the ΔNO was 187 ppm. Between 40 and 50 minutes on line, the absorption dropped back to 125 ppm NO. Similarly, the NO_2 absorption was complete for the first 40 minutes; however, during the last ten minutes on line the absorption rapidly dropped to 150 ppm. The last run shown in the table lasted for two hours. During the first 70 minutes, the SO_2 absorption gradually dropped from 500 ppm to 440 ppm. This trend continued until the end of the two hours when the absorption of SO_2 rapidly decreased to almost zero. This is probably due to saturation and the decline in pH.

The sulfate formation occurring in the $CaSO_3$ experiments is shown in Table 11.

TABLE 11

SULFATE FORMATION IN $CaSO_3$ SLURRIES

Initial pH	7.2	8.0	12	7.6 (SO_2 in Flue Gas)
Wt. % $SO_4^=$ (t = o)	0.29	0.18	0.16	0.16
Wt. % $SO_4^=$ (t = 25 min)	0.33	0.23	0.45	--
Wt. % $SO_4^=$ (t = 50 min)	0.36	0.31	--	0.51*
Δ_{50}	0.07	0.13	--	0.35

---

* Run lasted 70 minutes.

The higher pH's dropped rapidly with the introduction of flue gas so that no runs were made at constant acidity throughout the experiment. The trend in these data is to greater sulfate formation at the higher pH. The presence of SO_2 also increased the formation of sulfate.

2.3.2 Scrubbing Flue Gas Containing NO_2 and SO_2

The data of section 2.3.1.1 to 2.3.1.6 indicated that the addition of NO_2 to flue gas did not significantly improve NO absorption whereas NO_2 absorption by sulfite solutions appeared feasible assuming the NO_x could be oxidized to NO_2 upstream from the scrubber. In order to explore NO_2-SO_2 absorption, several solutions and slurries were screened for scrubbing potential.

2.3.2.1 NO_2- SO_2 Absorption by Sulfites

Sulfur dioxide readily dissolves in alkaline solutions but not in acids. The sulfite solutions are more or less basic depending on the solubility of the salt. The hydrolysis of the soluble sulfite ion raises the pH.

$$SO_3^= + H_2O \rightleftharpoons HSO_3^- + OH^-$$

Flue gas contains approximately 12 volume % CO_2 which is also soluble in alkaline solutions, but because of the relative acid strengths of H_2SO_3 and H_2CO_3, there is a range of pH where SO_2 is quite soluble whereas CO_2 is only slightly so. This range, which is around pH 7, would be optimum for scrubbing NO_2-SO_2. The absorption of NO_2 by sulfites is not sensitive to pH.

Several sulfite scrubbers were screened for simultaneous NO_2-SO_2 scrubbing. Table 12 contains a summary of the results.

TABLE 12

NO_2-SO_2 ABSORPTION BY SULFITES

Exp. #	Absorbent	Input (ppm)		% Absorption		Solution	pH		Run Time
		NO_2	SO_2	NO_2	SO_2	Temp. (°F)	Initial	Final	(min)
3-13-72	$CaSO_3$ Slurry (8 g/l)	330	500	60	92	125	7.6	5.0	70
3-30-72	$MgSO_3$ (5 g/l)	690	2610	100→45	100	126	9.4	3.7	40
4-3-72	$CaSO_3$ Slurry (25 g/l)	860	1890	100	100	126	9.1	7.2	75
4-24-72	2m NH_4HSO_3 0.5m $(NH_4)_2SO_4$	700	2370	94	83	122	5.9	5.9	145
6-22-72	$(NH_4)_2SO_3$ Mixture*	500 + (450 NO)	2860	100 + (22% NO)	97	128	6.3	6.3	70

---

* Mixture consisted of 11.2 Wt. % NH_4HSO_3, 14.6 Wt. % $(NH_4)_2SO_3$, 16.6 Wt. % $(NH_4)_2SO_4$, and 57.6 Wt. % H_2O. The specific gravity was 1.24.

The SO_2 removal was good in all the runs but the NO_2 absorption varied with the amount soluble sulfite present. After going on line, the pH of the $CaSO_3$ slurry in run # 3-13-72 dropped to 5.3 within 30 minutes. This run was continued for 290 minutes and at 115 minutes the slurry became saturated with SO_2. When SO_2 broke through, its value exceeded the input level for about an hour, then gradually decreased to slightly less than the input value. Apparently, some of the sulfite or bisulfate evolved SO_2 for a short while. With a greater solids loading in the slurry as in run # 4-3-72, the absorption of NO_2 and SO_2 was improved.

The sulfite in the $MgSO_3$ experiment may have been rapidly depleted by the O_2 in the flue gas. This would account for the continuous decrease in NO_2 absorption during the run. The original sulfite level was 0.08 molar ($MgSO_3$ is quite soluble).

The last two runs listed in Table 12 again indicate that the presence of sulfate does not inhibit NO_2 absorption as long as sufficient sulfite ion is available. Run # 6-22-72 also included NO in the flue gas which reaffirmed the earlier conclusion that sulfites are not attractive NO absorbants.

2.3.2.2 NO_2-SO_2 Absorption by Hydroxides and Carbonates

Several metal hydroxide slurries were screened for NO_2-SO_2 scrubbing potential. In addition, a limestone ($CaCO_3$) slurry was investigated. Since magnesia, lime and limestone scrubbing systems are presently under consideration for SO_2 scrubbing, the results on the combined scrubbing are significant. A summary of results is contained in Table 13.

The results show these slurries to be less efficient for NO_2 scrubbing than the sulfite slurries and solutions. However, they exhibit excellent absorption of SO_2. The presence of SO_2 is vital for NO_2 absorption as indicated by the two runs numbered 3-17-72. Only 19% of the NO_2 was absorbed in the absence of SO_2 wherease 50% was scrubbed out in its presence Thus, the sulfite formed during SO_2 scrubbing becomes the absorbent for NO_2.

A NO_x material balance was measured at the end of run #3-22-72, which employed a $Mg(OH)_2$ slurry. Gas analysis indicated 6.9 millimoles of NO_2 removed. Solution analysis showed 6.1 millimoles of NO_3^- and 2.0 millimoles of NO_2^- produced. Nitrate ion is the main product of NO_2 absorption from flue gas.

All of the slurries demonstrated roughly equal scrubbing efficiency on the full flue gas. When oxygen was eliminated from the gas stream, the scrubbing efficiency improved markedly. For example, during run # 4-10-72 the O_2 was removed from the stream with the result that the NO_2 absorption increased from 63% to 90%. With the oxygen flow turned on, the NO_2 absorption dropped back to 69%. Similar effects were observed with the other slurries. The presence of hydroquinone, an anti-oxidant, diminished the negative influence of oxygen upon NO_2 absorption. Run # 4-18-72 provides an example. A flue gas containing 670 ppm NO_2 and 2400 ppm SO_2 but no O_2 was bubbled into an $Mg(OH)_2$ slurry. All of the NO_2 and SO_2 was absorbed. When 3% oxygen was added to the flue gas, the NO_2 absorption dropped to 57% while the SO_2 continued to be totally removed. The addition of 1.0 gram of HQ to the slurry instantly caused the NO_2 absorption to increase to 93% in the presence of oxygen. The HQ was still effective 200 minutes later, when the run was terminated. Similar effects were observed with other slurries but were not as dramatic. An endurance run (#5-5-72) was made with a slurry containing 15g of $Mg(OH)_2$ and 1.0 gram of HQ. The flue gas contained 675 ppm NO_2, 2280 ppm SO_2 and 3% O_2 in addition to the normal constituents. The SO_2 absorption was complete for the full 390 minutes of the run. The NO_2 absorption was about 100% during the first 200 minutes of the run but gradually decreased to 82% at the end of the experiment. The slurry slowly turned yellow as the run progressed. The HQ is acting as an oxidation inhibitor but undergoes slow degradation, perhaps due to reaction with NO_2.

TABLE 13

NO_2-SO_2 ABSORPTION BY HYDROXIDES AND CARBONATES

Exp. #	Absorbent	Input (ppm)		% Absorption		Solution Temp. (°F)	pH		Run Time (min)
		NO_2	SO_2	NO_2	SO_2		Initial	Final	
3-17-72	$Ca(OH)_2$ slurry (10 g/1)	740	0	19	--	132	11.2	6.6	50
3-17-72	(continuation of 3-17-72)	730	800	50	81	132	6.6	6.0	70
4-10-72	$Ca(OH)_2$ slurry (15 g/1)	700	2490	63	100	126	11.2	6.4	80
4-7-72	$Ca(OH)_2$ slurry (18 g/1)	680	2460	56	100	125	11.2	6.5	40
3-22-72	$Mg(OH)_2$ slurry 7.4 (g/1)	830	2460	58	100	126	8.7	7.8	110
4-7-72	$Mg(OH)_2$ slurry 14 (g/1)	680	2610	56	100	126	9.3	7.9	100
4-10-72	ZnO slurry (10 g/1)	700	2490	63	100	126	9.3	6.3	40
4-14-72	$CaCO_3$ slurry (10 g/1)	650	2280	46	100	128	7.5	6.2	100
4-14-72	$CaCO_3$ slurry (4 g/1)	650	2280	46	100	128	7.2	6.3	60

Several experiments were conducted in order to determine sulfate formation during $Mg(OH)_2$ scrubbing. These results are compared with similar $CaSO_3$ scrubbing data in Table 14.

TABLE 14

SULFATE FORMATION IN $Mg(OH)_2$ SLURRIES

	[a]$Mg(OH)_2$	[b]$Mg(OH)_2$	[c]$Mg(OH)_2$	[d]$CaSO_3$
Wt. % $SO_4^{=}$ (t = o min)	0.005	0.019	0.0079	0.16
Wt. % $SO_4^{=}$ (t = 100 min)	0.181	0.230	0.202	0.51*
Δ_{100}	0.176	0.211	0.194	0.35*
millimoles of $SO_4^{=}$ formed	18.6	22.2	20.5	37
millimoles of NO_2 absorbed	5.2	4.9	8.7	2
millimoles of SO_2 absorbed	31	30	31	4.5

---

* 70 minutes on line.

[a] Contained 15g $Mg(OH)_2$ per liter; SO_2 absorption was 2400 ppm; NO_2 absorption was 400 ppm out of 700 ppm input.

[b] Same as above except that the SO_2 absorption was 2300 ppm; NO_2 absorption was 380 out of 640 ppm input.

[c] Same as in footnote 'a' except that the NO_2 absorption was 670 ppm out of 670 ppm input and the flue gas contained no oxygen.

[d] Contained 8g $CaSO_3$ per liter; SO_2 absorption was 500 ppm and the NO_2 absorption was 220 ppm out of 340 ppm.

Of the several absorbents, the $CaSO_3$ formed the most sulfate. Absorbent 'c' which scrubbed an O_2-free flue gas, formed as much sulfate as the other $Mg(OH)_2$ slurries did in the presence of 3% oxygen. However 'c' absorbed almost twice as much NO_2 so that the number of sulfates formed per unit NO_2 absorbed is lower than the other two. The data show that 2/3 of the SO_2 absorbed by the magnesia absorbents is converted to sulfate.

2.3.3 Miscellaneous Scrubbing Experiments

This section contains a variety of scrubbing experiments that did not fit into the discussions above. Table 15 presents the results.

TABLE 15

NO_x-SO_2 SCRUBBING

Exp. #	Absorbent	Input ppm			% Absorption			Solution Temp. (°F)	Run Time (min)
		NO	NO_2	SO_2	NO	NO_2	SO_2		
2-2-72	Hydroquinone (1. g/1)	0	360	0	(gen)[a]	47	--	124	70
3-24-72	$FeCl_3 \cdot 6H_2O$ (5. g/1)	490	0	0	2	--	--	122	100
3-24-72	3% H_2O_2	490	0	0	4	--	--	85	40
3-24-72	$KMnO_4$ (4 g/1)	475	0	0	63	(gen)[b]	--	80	30
4-13-72	1.88m Na_2S	0	650	2250	(gen)[c]	100	95	131	80
5-15-72	2.1m Na_2S	0	370	0	(gen)[d]	100	--	125	60
5-3-72	3.8m Urea	480	0	0	3.1	--	--	122	10
5-3-72	3.8m Urea	490	0	2150	0	--	70	122	20
5-3-72	3.8m Urea	325	400	2160	7.7	37	70	122	15
5-2-72	0.47m Urea in 40% HNO_3	475	0	0	42	(gen)[e]	--	135	75
5-9-72	1000 g of 10% Urea sol'n + 360ml 6N H_2SO_4	520	0	0	0	--	--	125	30

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[a] Absorption of 170 ppm NO_2 generated 180 ppm NO.

[b] Generated approximately 30 ppm NO_2.

[c] Generated 35 ppm NO.

[d] Generated 23 ppm NO.

[e] Absorbed 200 ppm NO and generated 360 ppm NO_2. If NO reacted with HNO_3 to produce NO_2 [$NO + 2HNO_3 \rightarrow 3NO_2 + H_2O$], 600 ppm NO_2 should have been generated. We have other data, however, to indicate that urea in HNO_3 absorbs approximately 45% of input NO_2 with negligible production of NO. This indicates that we should expel roughly 325 ppm NO_2 into the effluent. This is reasonably close to what we observed.

A solution of HQ was observed to reduce NO_2 to NO almost quantitatively. The only scrubber that was found capable of successfully absorbing NO alone contained 4 grams of potassium permanganate. The solution gradually changed color from deep purple to deep brown. This appears to be due to the formation of lower oxides of manganese. A slurry of MnO_2 was found to have no effect upon NO absorption. The same was true for a sodium arsenate solution (Na_2HAsO_4).

Sodium sulfide solutions were excellent NO_2 absorbents but generated a small amount of NO. The sulfide appears to become oxidized to sulfur which forms polysulfide ion in the presence of excess sulfide. A small amount of spent absorbent was acidified with HCl which destroyed the polysulfide ion and produced a milky precipitate of colloidal sulfur. When SO_2 was absorbed by Na_2S solutions, some H_2S was generated. An attempt was made to analyze the spent solution for nitrate and nitrite levels but spectral interference by species in solution precluded this approach.

Several experiments were conducted with urea under a variety of conditions, however, none showed any promise.

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3. CONCLUSIONS AND RECOMMENDATIONS

3.1 Conclusions

A comprehensive screening program was instituted in order to evaluate the capability of various aqueous systems to scrub NO_x from the flue gases emitted by stationary power plants fired with fossil fuels. The conclusions of this study are listed as follows:

(1) NO and NO_2 present in the flue gas but no SO_2

   (a) Slurries and solutions of calcium, magnesium, and zinc hydroxide are very inefficient.

   (b) Strong acid (H_2SO_4) and strong base (NaOH) are poor NO_x absorbents.

   (c) Concentrated amines (ammonia and 2-aminoethanol) are efficient NO_x absorbents but they have excessive vapor pressures (28 wt % NH_4OH) and may form exotic products such as alkyl nitrites and nitrates, and nitro and nitroso compounds which are difficult to regenerate and could not be introduced safely into the environment.

   (d) Potassium premanganate solutions are excellent absorbents of NO even in the absence of NO_2. However, regeneration of the spent solution appears to be a formidable obstacle.

   (e) Sulfite solutions and slurries are excellent NO_2 but poor NO absorbents. The soluble sulfites are more effective NO_2 absorbents than the insoluble slurries because of the higher sulfite levels attained in solution.

   (f) In general, NO_2 recycle and addition to flue gas to achieve equimolar NO/NO_2 is not attractive. While the presence of NO_2 does increase the absorption of NO, the magnitude of the increase is insufficient for developing a viable process.

(2) NO_2 and SO_2 present in the flue gas but no NO

   (a) Calcium, magnesium and zinc hydroxides are effective NO_2 and SO_2 absorbents. The sulfite formed when SO_2 is absorbed is vital to NO_2 scrubbing.

   (b) Limestone is an effective NO_2/SO_2 absorber.

   (c) Sulfite solutions and slurries are efficient NO_2-SO_2 absorbers.

   (d) NO_2 scrubbing is enhanced by removing oxygen from the flue gas or by adding an anti-oxidant such as hydroquinone to the scrubber.

(e) A portion of the absorbed SO_2 is oxidized to sulfate.

(f) Sulfide solutions are excellent NO_2 and SO_2 absorbers but do generate a small amount of NO.

(g) Combined NO_x - SO_x scrubbing is possible using any of several hydroxide or carbonate systems provided NO can be oxidized to NO_2 upstream from the scrubber.

(h) Separate NO_2 absorption is feasible using the sulfite solution or slurry produced in the SO_2 scrubber.

Several scrubbing systems appear promising with a high degree of flexibility available in their application. However, this hypothesis must be supported by further research aimed at obtaining scale-up information in addition to spent-solution regeneration data.

3.2 Recommendations for Future Work

Our results clearly indicate the technical feasibility of modifying any of several aqueous alkaline flue gas desulfurization systems, now being developed, to incorporate NO_x emissions control. These include aqueous ammonia, limestone, magnesium hydroxide, and sodium hydroxide based systems. Pilot plant studies are now needed, however, to develop the engineering data essential for process scale-up. Below are listed critical factors which need to be defined under process conditions.

- The rates of NO_2 absorption by different alkaline solutions and slurries need measuring under pilot plant conditions. The influence of system parameters, such as temperature and flow rates, upon the NO_2 absorption rates must be determined.
- The effect of scrubber design upon the gas absorption must be defined.
- The requirements for anti-oxidants must be assessed.
- The product distribution for the absorbed NO_x (i.e., NO_3- vs NO_2-) must be measured.
- The study of spent-solution regeneration will require a comprehensive effort in order to define sorbent make-up requirements and the power, fuel and other utility needs.
- The oxidation of NO_x to NO_2 upstream from the scrubber is vital to the project. Thus, studies should be instituted to optimize this reaction under flue gas conditions using catalysts or ozone.

The final goal would be to successfully couple the NO_x oxidation, scrubbing, and solution regeneration techniques into an integrated process which cleans flue gas and simultaneously minimizes the effect of scrubbing products upon the environment.

APPENDIX A

This appendix contains idealized thermodynamic calculations for the energy required to regenerate certain species found in spent sorbents.

A.1 Electrochemical Reduction of Sulfate to Sulfite

Sulfate is formed during flue gas scrubbing via oxidation of sulfite by the NO_x or O_2 present. In order to regenerate sulfite, which is useful for NO_2 absorption, from sulfate, the following electrochemical calculations are informative.

$$\begin{array}{lr} & E^\circ_{298} \\ 4OH^- \longrightarrow O_2 + 2H_2O + 4e^- & -0.40 \text{ volts} \\ SO_4^= + H_2O + 2e^- \longrightarrow 2OH^- + SO_3^= & -0.94 \text{ volts} \end{array}$$

When these half-cells are summed, we obtain

$$2SO_4^= \longrightarrow O_2 + 2SO_3^= \qquad -1.33 \text{ volts}$$

Since the electrical work required, assuming no overvoltage, is equal to the Gibbs free energy of the reaction, we have

$$\begin{aligned} \Delta G = nFE &= 61.\ \text{kcal per mole of } SO_4^= \\ &= 0.071 \text{ kwh per mole of } SO_4^= \end{aligned}$$

If we consider 10^6 SCF of flue gas from which 400 ppm NO_x are scrubbed, we calculate that 32.3 kwh are needed to regenerate the sulfite assuming that one $SO_4^=$ is formed per NO_x absorbed. This number represents an idealized regeneration which may be scaled up or down depending on the amount of NO_x absorbed and the number of sulfates formed per NO_x absorbed.

A.2 Thermal Regeneration of MgO from $MgSO_4$

Since sulfate is formed in NO_x-SO_2 scrubbers using magnesia as the absorbent, it is of interest to calculate the theoretical energy requirements for the thermal regeneration of MgO from $MgSO_4$.

$$\begin{array}{lcl} MgSO_4(s) & \xrightarrow{\Delta} & MgO(s) + SO_3(g) \\ -306 \text{ kcal} & & -144 \text{ kcal} \quad -95 \text{ kcal} \end{array}$$

$$\Delta H = 67 \text{ kcal/mole}$$

If water of hydration is included in the calculation, then an additional reaction must be considered.

$$MgSO_4 \cdot 6H_2O(s) \xrightarrow{\Delta} MgSO_4(s) + 6H_2O(g)$$
$$-737 \text{ kcal} \qquad -306 \text{ kcal} \quad -348 \text{ kcal}$$
$$\Delta H' = 83 \text{ kcal/mole}$$

The total theoretical energy required is 67 kcal per mol of anhydrous $MgSO_4$ and 150 kcal/mole of the hexahydrate. This translates into 0.078 (0.175) kwh per mole of sulfate formed. The numbers in parentheses refer to the hexahydrate. If we scrub 10^6 SCF of flue gas from which 400 ppm NO_x are absorbed and assume the one mole of sulfate is formed per mole of NO_x absorbed, we require 35.8 (80.4) kwh for regeneration. If we scrub 10^6 SCF of flue gas and remove 700 ppm NO_x and form 10 moles of sulfate per mole of NO_x absorbed then 626 (1400) kwh are needed for regeneration.

A.3 Thermal Regeneration of MgO from $MgSO_3$

Magnesium sulfite is produced by the absorption of SO_2 by $Mg(OH)_2$ slurries. Magnesium oxide may be thermally regenerated from the sulfite.

$$MgSO_3(s) \xrightarrow{\Delta} MgO(s) + SO_2(g)$$
$$-241 \text{ kcal} \qquad -144 \text{ kcal} \; -71 \text{ kcal}$$
$$\Delta H = 26 \text{ kcal/mole}$$

$$MgSO_3 \cdot 6H_2O(s) \longrightarrow MgSO_3(s) + 6H_2O(g)$$
$$-673 \text{ kcal} \qquad -241 \text{ kcal} \quad -348 \text{ kcal}$$

Regeneration requires 26 (110) kcal per mole of sulfite formed. The numbers in parentheses refer to the hydrate. This is 0.030 (0.130) kwh per mole of sulfite. If 3000 ppm SO_2 are scrubbed from 10^6 SCF of flue gas the theoretical energy required for regeneration of MgO is 103.5 (448) kwh.

APPENDIX B

Herein are contained the experimental results depicted in graphical form. This style of presentation was chosen because it reflects the form in which the data was originally recorded. The continuous line presentation also communicates data trends to the reader more effectively than does the tabular format. The leters 'BP' signify that the flue gas by-passed the scrubber.

Following each graph is a data sheet which gives the flue gas composition, solution composition, and temperature, pH, etc. At the bottom of each data sheet is a notation which indicates the sequence of traps which treated that portion of the scrubber effluent going into the NO analyzer. For example,

$$\text{NO: } Na_2SO_3 \longrightarrow \text{Dry Ice} \longrightarrow \text{NDIR}$$

signifies that part of the scrubbed gas bubbled through a saturated solution of Na_2SO_3 (to remove residual NO_2), then passed through a dry ice cold trap (to remove water vapor) and finally entered the Beckman Non-Dispersive Infra-Red (NDIR) nitric oxide analyzer. Some NO was absorbed by the various traps employed but all were calibrated with known gas compositions before going on line.

The following listing is an index to the data contained in this appendix.

INDEX TO SCRUBBING EXPERIMENTS

Run #	Input NO	 NO_2	 SO_2	Absorbent Composition	Page
11-9-71	X	X		water	
11-10-71	X	X		water	
11-12-71	X	X		water	
11-16-71	X	X		water	
11-17-71	X	X		water	
11-18-71	X	X		water	
11-19-71	X	X		5N NaOH	
11-22-71	X	X		83 wt.% H_2SO_4	
12-3-71	X	X		79 wt.% H_2SO_4	
12-5-71a	X	X		5N NaOH	
12-5-71b	X	X		4.1m$(NH_4)_2SO_3$	
12-7-71	X	X		NaOH(pH=11.5)	
12-13-71	X	X		$Mg(OH)_2$ solution (pH=8.9)	
12-15-71	X	X		$Zn(OH)_2$ solution (pH=7.5)	
12-17-71	X	X		NaOH(pH=8.9)	
12-20-71	X	X		$Ca(OH)_2$ solution (pH=11.5)	
12-21-71	X	X		sat'd Na_2SO_3 in 5N NaOH	
1-3-72	X	X		sat'd Na_2SO_3	
1-10-72	X	X		NH_4HSO_3 + NH_4HSO_4	
1-17-72	X	X		6m NaOAc	

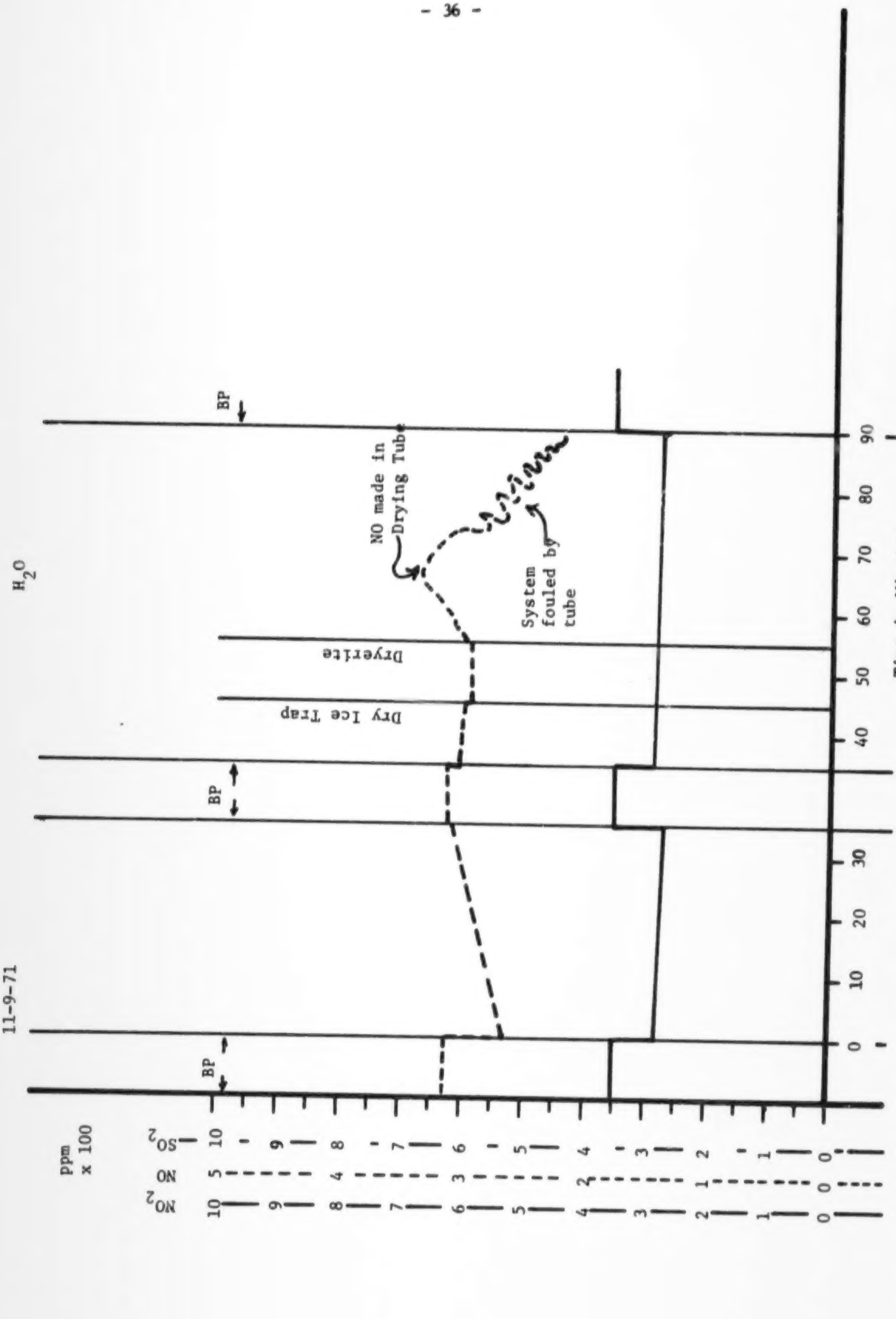
INDEX TO SCRUBBING EXPERIMENTS (Cont'd)

Run #	Input			Absorbent Composition	Page
	NO	NO_2	SO_2		
1-18-72	X	X		8.4m NH_4Cl	
1-19-72	X	X		28 wt.% NH_4OH	
1-19-72	X	X		Glacial acetic acid	
1-19-72	X	X		50 wt.% NaOH	
1-24-72	X	X		8.4m NH_4OAc	
1-25-72	X	X		7.m NH_4OAc	
1-26-72	X	X		28 wt.% NH_4OH	
1-27-72	X	X		14.8m NaOH	
1-28-72	X	X		2.3m Na_2SO_3	
1-31-72	X	X		2.3m Na_2SO_3 + hydroquinone (HQ)	
2-1-72	X	X		Varying Na_2SO_3 + NH_4SO_3	
2-2-72	X	X		Hydroquinone (HQ)	
2-3-72	X	X		2-aminoethanol (2AE)	
2-4-72	X	X		2AE + H_2O (1:1)	
2-4-72	X	X		2AE + H_2O (1:3)	
2-8-72	X	X		$Ca(OH)_2$ slurry	
2-9-72	X	X		ZnO slurry	
2-9-72	X	X		$Mg(OH)_2$ slurry	
2-10-72	X	X		1.0m ammonium citrate	
2-15-72	X	X		2.5m Na_2SO_3 + HQ	
2-18-72	X	X		2.5m Na_2SO_3	
3-3-72	X	X		1.0m Na_2SO_3 (vary pH)	
3-7-72	X	X		$CaSO_3$ slurry (vary pH)	
3-8-72	X	X		2-aminoethanol	
3-10-72		X	X	SO_2-NO_2 interaction in lines	
3-13-72		X	X	$CaSO_3$ slurry	
3-15-72		X	X	CaO + $CaSO_3$ slurry	
3-16-72		X	X	$Ca(OH)_2$ slurry	
3-17-72		X	X	$Ca(OH)_2$ slurry	
3-22-72		X	X	$Mg(OH)_2$ slurry	
3-24-72	X			$FeCl_3$, H_2O_2, $KMnO_4$	
3-30-72		X	X	$MgSO_3$	
4-5-72		X	X	$CaSO_3$ slurry	
4-7-72		X	X	$Mg(OH)_2$ slurry	
4-7-72		X	X	$Ca(OH)_2$ slurry	
4-10-72		X	X	$Ca(OH)_2$ slurry	
4-10-72		X	X	ZnO slurry	
4-11-72		X	X	$Ca(OH)_2$ pre-doped with SO_2	
4-13-72		X	X	1.88m Na_2S	
4-14-72		X	X	$CaCO_3$ slurry	
4-17-72		X	X	H_2O + $CaCl_2$, $MgSO_4$	
4-18-72		X	X	$Mg(OH)_2$ slurry + HQ	
4-24-72		X	X	2m NH_4HSO_3 + 0.5m $(NH_4)_2SO_4$	
4-25-72		X	X	2m NH_4HSO_3 + 0.5m $(NH_4)_2SO_4$	
4-25-72	X	X		30 wt.% H_2SO_4	
4-26-72		X	X	$Mg(OH)_2$ slurry + HQ	
4-27-72		X	X	$Mg(OH)_2$ slurry + HQ	

INDEX TO SCRUBBING EXPERIMENTS (Cont'd)

Run #	Input NO	 NO_2	 SO_2	Absorbent Composition	Page
4-28-72		X	X	$CaCO_3$ slurry + HQ	
5-1-72		X	X	$Ca(OH)_2$ slurry + HQ	
5-2-72	X			Urea in HNO_3	
5-2-72	X	X		Urea in HNO_3	
5-2-72		X		Urea in HNO_3	
5-3-72	X			Urea in H_2O	
5-3-72	X		X	Urea in H_2O	
5-3-72	X	X		Urea in H_2O	
5-3-72	X	X	X	Urea in H_2O	
5-4-72	X	X	X	$Mg(OH)_2$ slurry	
5-5-72		X	X	$Mg(OH)_2$ slurry + HQ (endurance test)	
5-9-72	X			Urea in H_2SO_4	
5-9-72	X	X		Urea in H_2SO_4	
5-9-72		X		Urea in H_2SO_4	
5-9-72		X	X	Urea in H_2SO_4	
5-9-72	X	X	X	Urea in H_2SO_4	
5-15-72		X		2.1m Na_2S	
6-22-72	X	X	X	$(NH_4)_2SO_3$, NH_4HSO_3 mixture	

B.1 EMISSION DATA AND RUN SHEETS


ppm x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
11-9-71
H_2O
BP
BP
BP
Dry Ice Trap
Dryerite
NO made in Drying Tube
System fouled by tube
0 10 20 30 40 50 60 70 80 90
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 11-9-71 SCRUB: H_2O

OBJECT: Test water trap

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 130 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

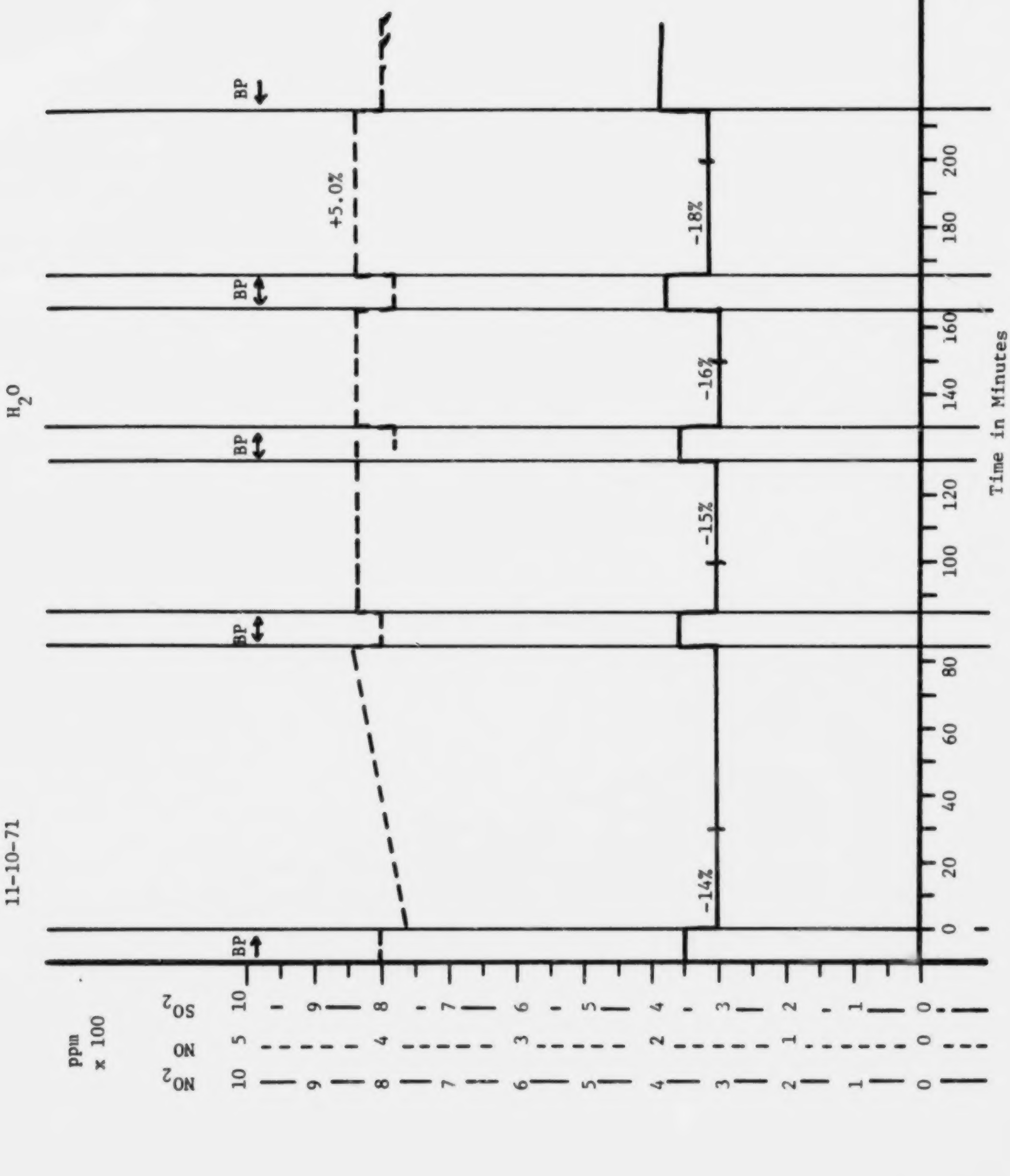
NO 312 ppm NO_2 350 ppm SO_2 -- ppm

COMMENT:

(1) Wet ice trap converts $\simeq$ 8% of the NO_2 to NO

(2) The dryerite converts $\simeq$ 11% of the $NO_2 \rightarrow NO$

NO: (wet ice, or dry ice, or Dryerite) → NDIR


11-10-71
H_2O
BP ↑
BP ↕
BP ↕
BP ↕
BP ↓
-14%
-15%
-16%
-18%
+5.0%
Time in Minutes
0
20
40
60
80
100
120
140
160
180
200
ppm x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 11-10-71 SCRUB: H_2O

OBJECT: Absorb NOX from flue gas

CONDITIONS: Scrub volume @ 1500 ~~1000~~ ml Total Gas Flow @ 3100 ~~3200~~ cm^3 per minute

Pot Temp. 125 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

NO 400 ppm NO_2 350 ppm SO_2 -- ppm

COMMENT:

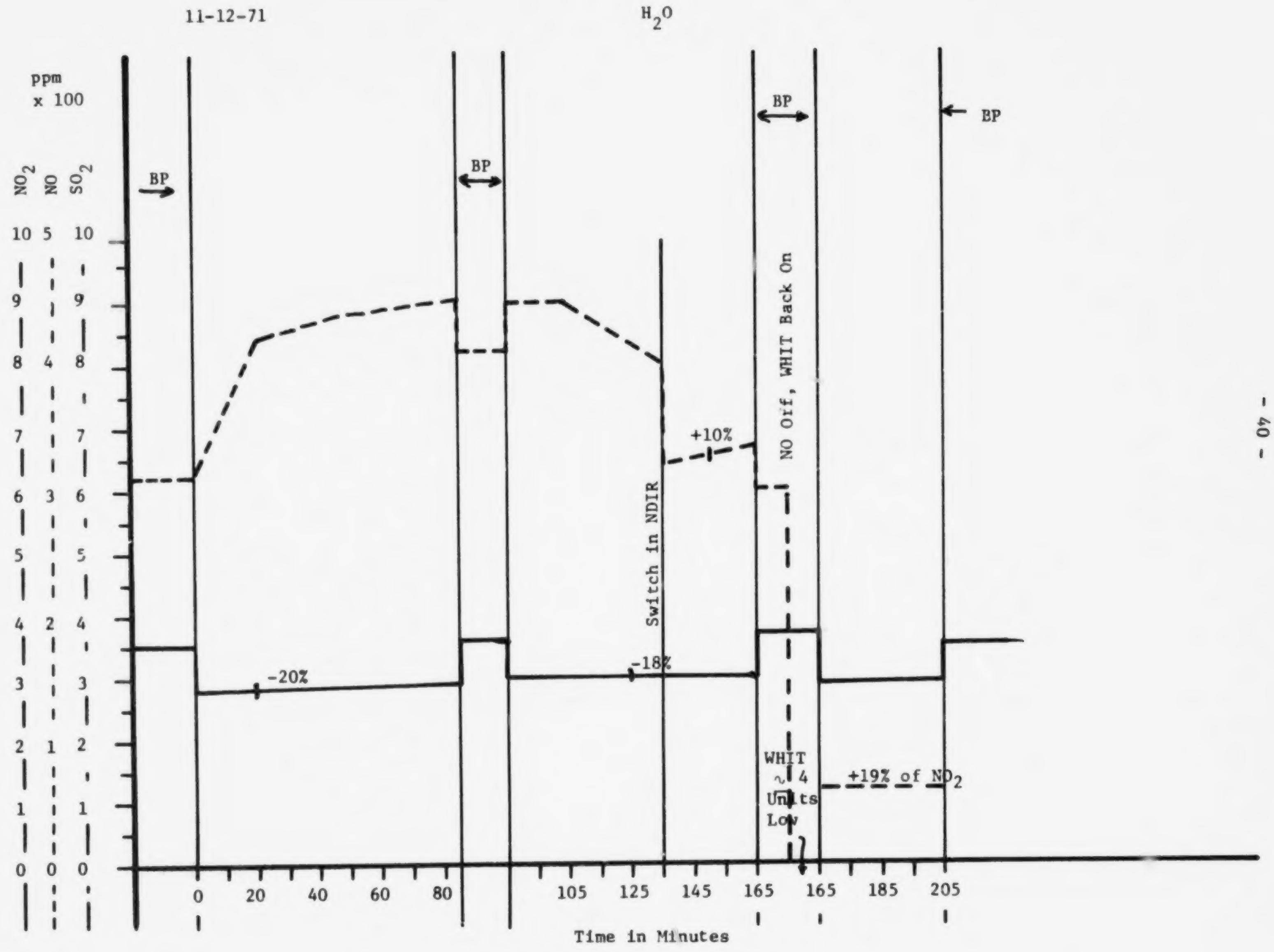
(1) After a slight initial absorption of NO, the water appears to hydrolyze the NO_2 and create some NO ($\approx$20 ppm out of 390 ppm NO_2 or 5% of the NO_2). NO_2 adsorption is relatively constant 14 → 18%

$$3NO_2 + H_2O \longrightarrow NO + 2HNO_3$$

If only hydrolysis occurred, $\approx$5% NO generation would correspond to 15% NO_2 adsorption.

(2) Solution sample taken at 215 minutes was analyzed by the nitrate ion electrode. Solution was 0.9×10^{-3} molar nitrite.

NO: Wet Ice Trap → Whit.


11-12-71
H_2O
ppm
x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
BP
BP
BP
-20%
-18%
+10%
Switch in NDIR
NO Off, WHIT Back On
WHIT
~ 4
Units
Low
+19% of NO_2
0
20
40
60
80
105
125
145
165
165
185
205
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 11-12-71 SCRUB: H_2O (from 11-10-71)

OBJECT: To compare the NDIR with the Whittaker "NOX BOX"

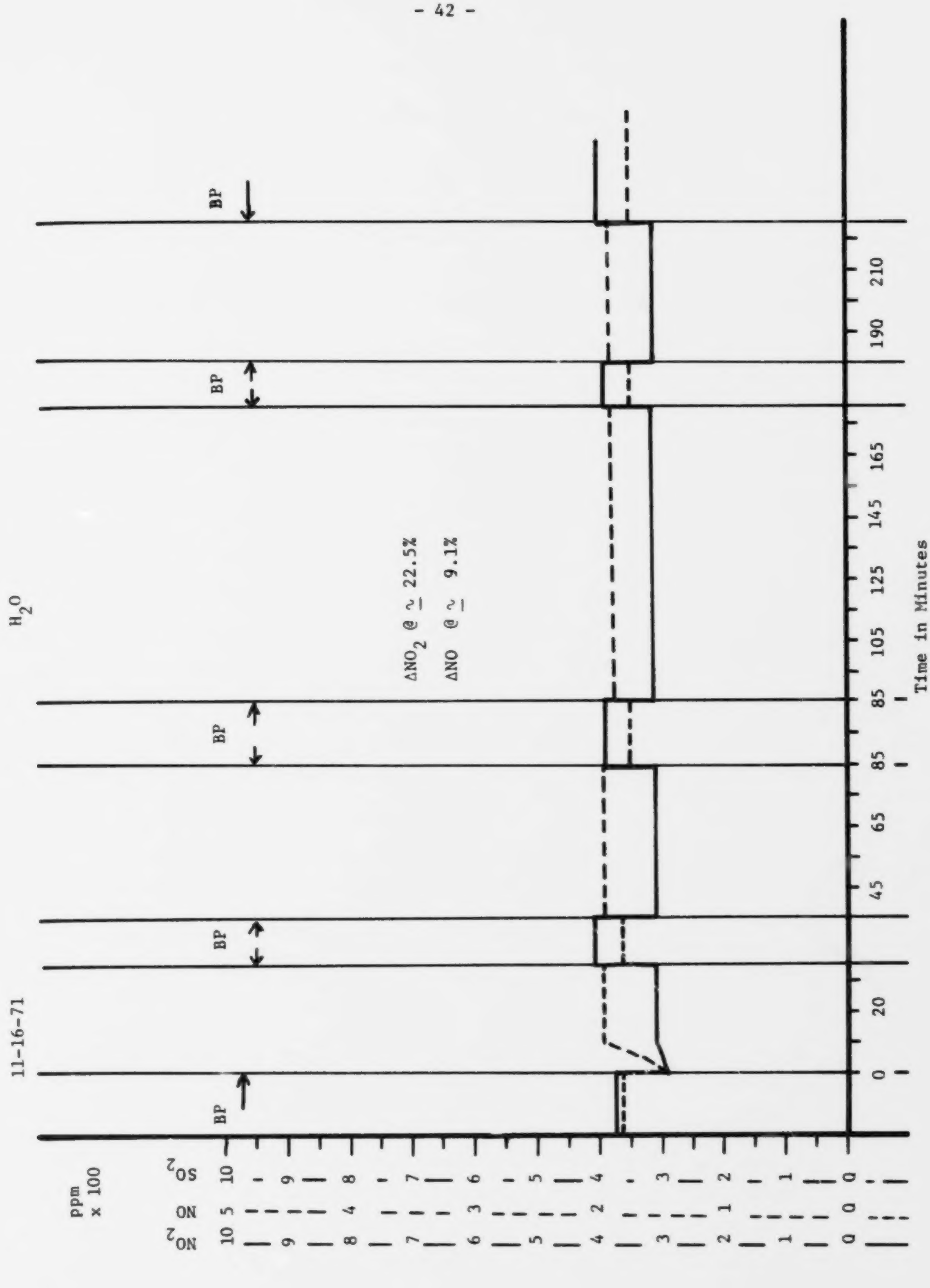
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	126 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	varies ppm	NO_2	350 ppm	SO_2	-- ppm

COMMENT:

(1) Already had 230 minutes (from 11-10-71) at zero time on chart.

NO: Wet Ice ⟶ NDIR


11-16-71
H_2O
ΔNO_2 @ ≃ 22.5%
ΔNO @ ≃ 9.1%
BP
BP
BP
BP
BP
Ppm
x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
0
20
45
65
85
85
105
125
145
165
190
210
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 11-16-71 SCRUB: H_2O

OBJECT: Absorb NOX and gain experience with system

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 123 °F Initial pH _____ Final pH _____

H_2O 10 % CO_2 12 % O_2 3 %

NO 180 ppm NO_2 370 ppm SO_2 -- ppm

COMMENT:

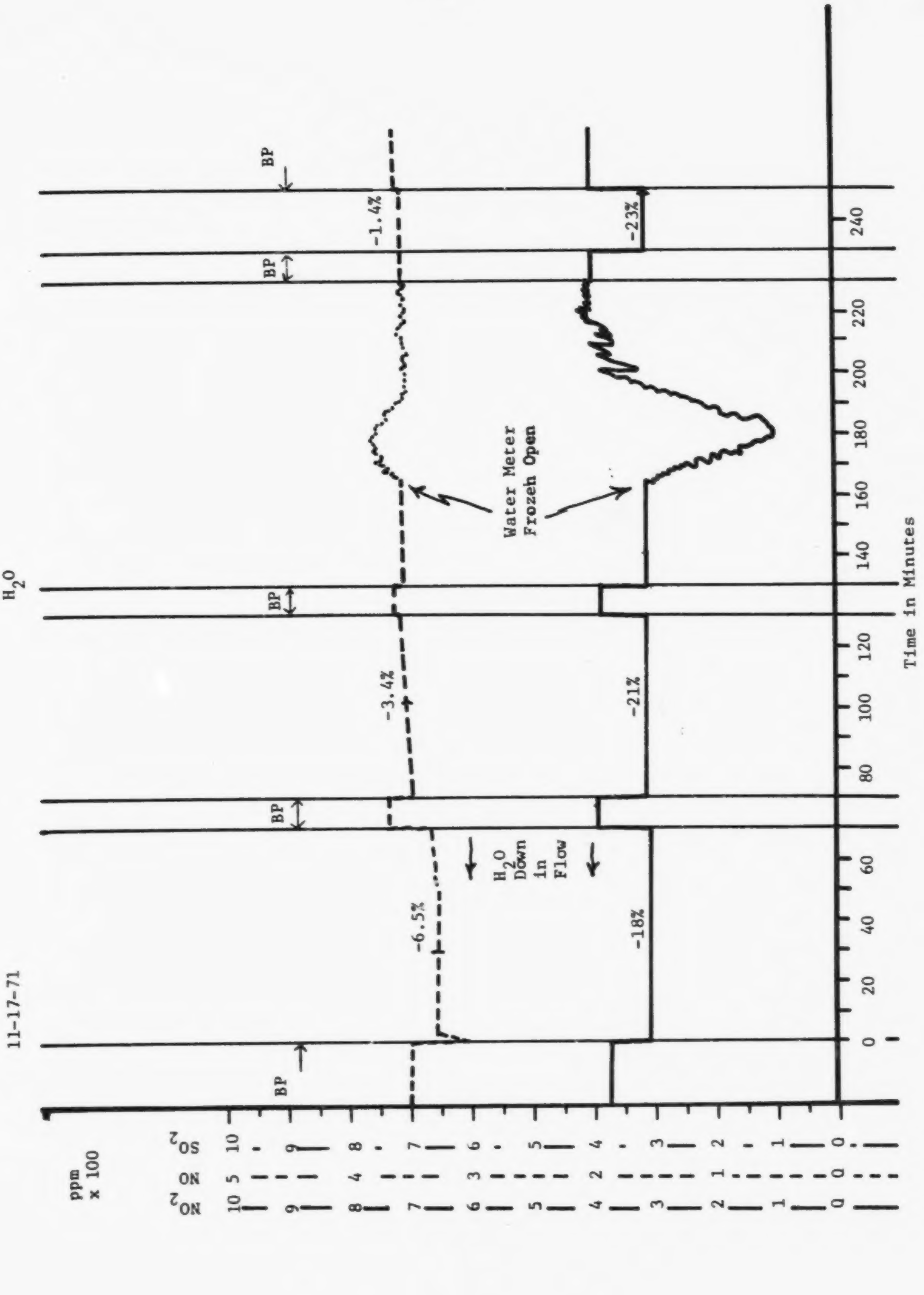
The scrub generated NO after 10 min. The NO generated (≅ 17 ppm) is 9.1% of the NO and 4.2% of the NO_2.

The reaction is:

$$3NO_2 + H_2O \longrightarrow NO + 2HNO_3$$

∴ 12.6% of the NO_2 adsorption is due to conversion

NO: Wet Ice Trap ⟶ NDIR


11-17-71
H_2O
ppm x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
BP
BP
BP
BP
BP
-6.5%
-18%
H_2O Down in Flow
-3.4%
-21%
Water Meter Frozen Open
-1.4%
-23%
0 20 40 60 80 100 120 140 160 180 200 220 240
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 11-17-71 SCRUB: H_2O

OBJECT: Absorb NOX and gain experience

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 129 °F Initial pH _____ Final pH _____

H_2O 10 % CO_2 12 % O_2 3 %

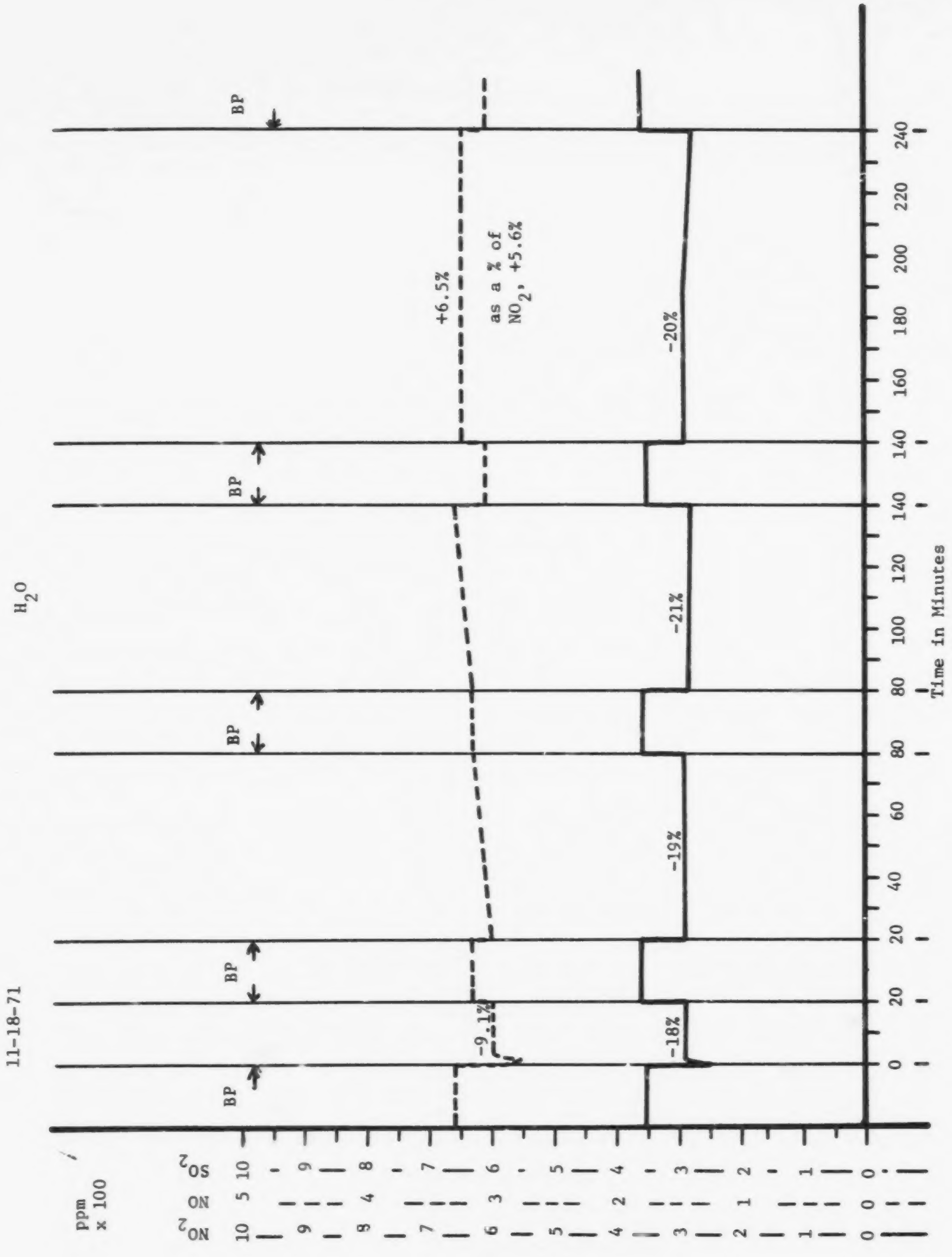
NO 348 ppm NO_2 370 ppm SO_2 -- ppm

COMMENT:

(1) The water meter was inconsistent and was sticking throughout the run.

(2) The NO was initially absorbed to ≃6-1/2%. This decreased to 1.4%. The NO_2 changed from 18% to 23%.

NO: Wet Ice Trap ⟶ NDIR


11-18-71
H$_2$O
BP
BP
BP
BP
BP
+6.5%
as a % of
NO$_2$, +5.6%
-9.1%
-18%
-19%
-21%
-20%
0
20
20
40
60
80
80
100
120
140
140
160
180
200
220
240
Time in Minutes
ppm
x 100
NO$_2$
NO
SO$_2$
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 11-18-71 SCRUB: H_2O

OBJECT: Absorb NOX and gain experience

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

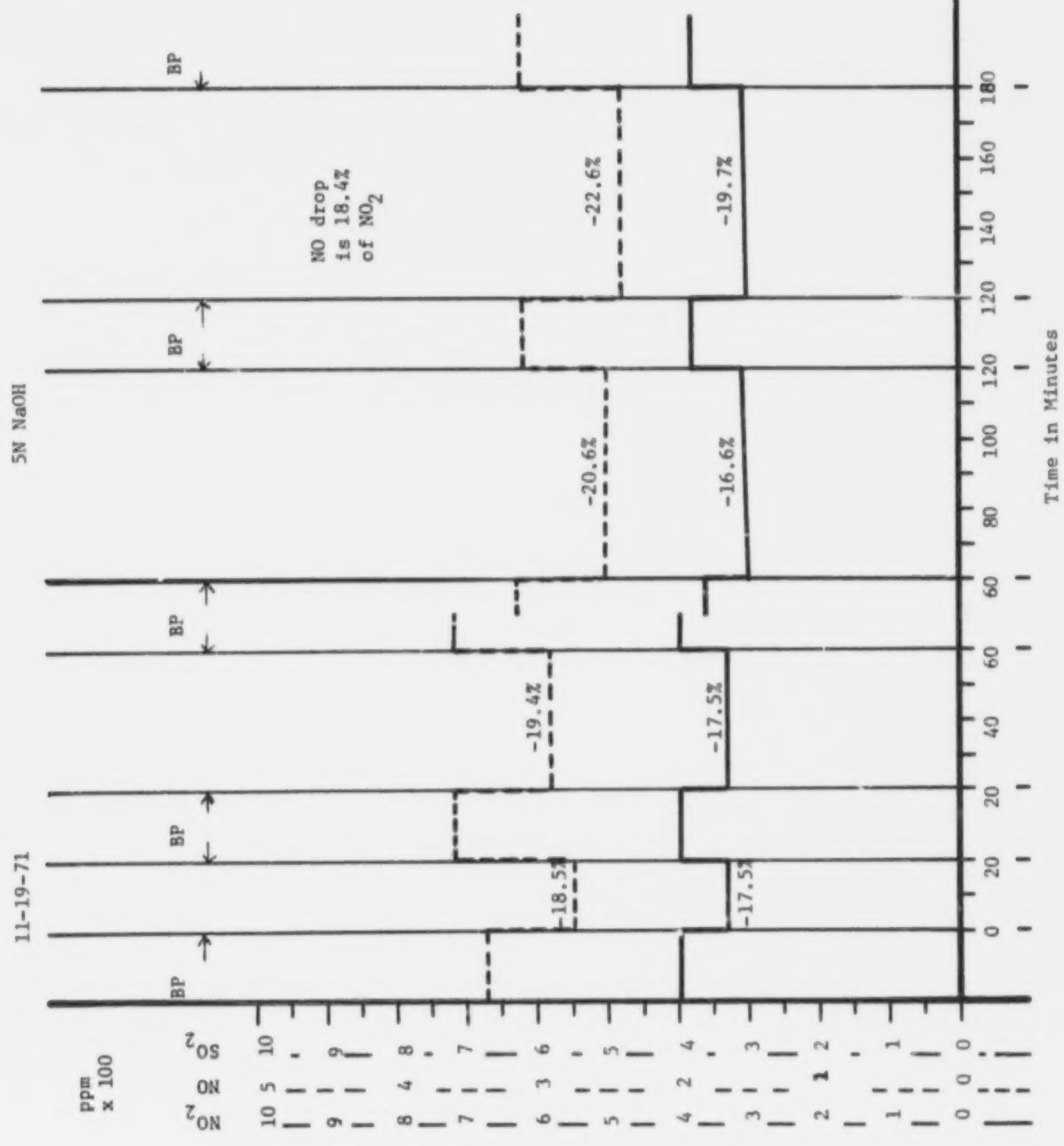
NO 360 ppm NO_2 330 ppm SO_2 -- ppm

COMMENT:

(1) In the beginning of the run, NO was absorbed to ≈ 9.1%. The system saturated with NO @ ≈ 80 min. (0%) and was producing 6.5% (5.6% as a frac. of NO_2) at the end of the run.

(2) The initial Δ NO_2 was 18%, the final 20%. Of the final Δ, 16.8% is accounted by $2NO_2 + H_2O \Rightarrow NO + 2HNO_3$

NO: Wet ice trap -> NDIR


11-19-71
5N NaOH
BP
BP
BP
BP
NO drop is 18.4% of NO$_2$
-18.5%
-17.5%
-19.4%
-17.5%
-20.6%
-16.6%
-22.6%
-19.7%
0
20
20
40
60
60
80
100
120
120
140
160
180
Time in Minutes
ppm x 100
SO$_2$
NO
NO$_2$
10
9
8
7
6
5
4
3
2
1
0
5
4
3
2
1
0

NOX SCRUBBING DATA SHEET

DATE: 11-19-71 SCRUB: 5N NaOH

OBJECT: NOX Absorption

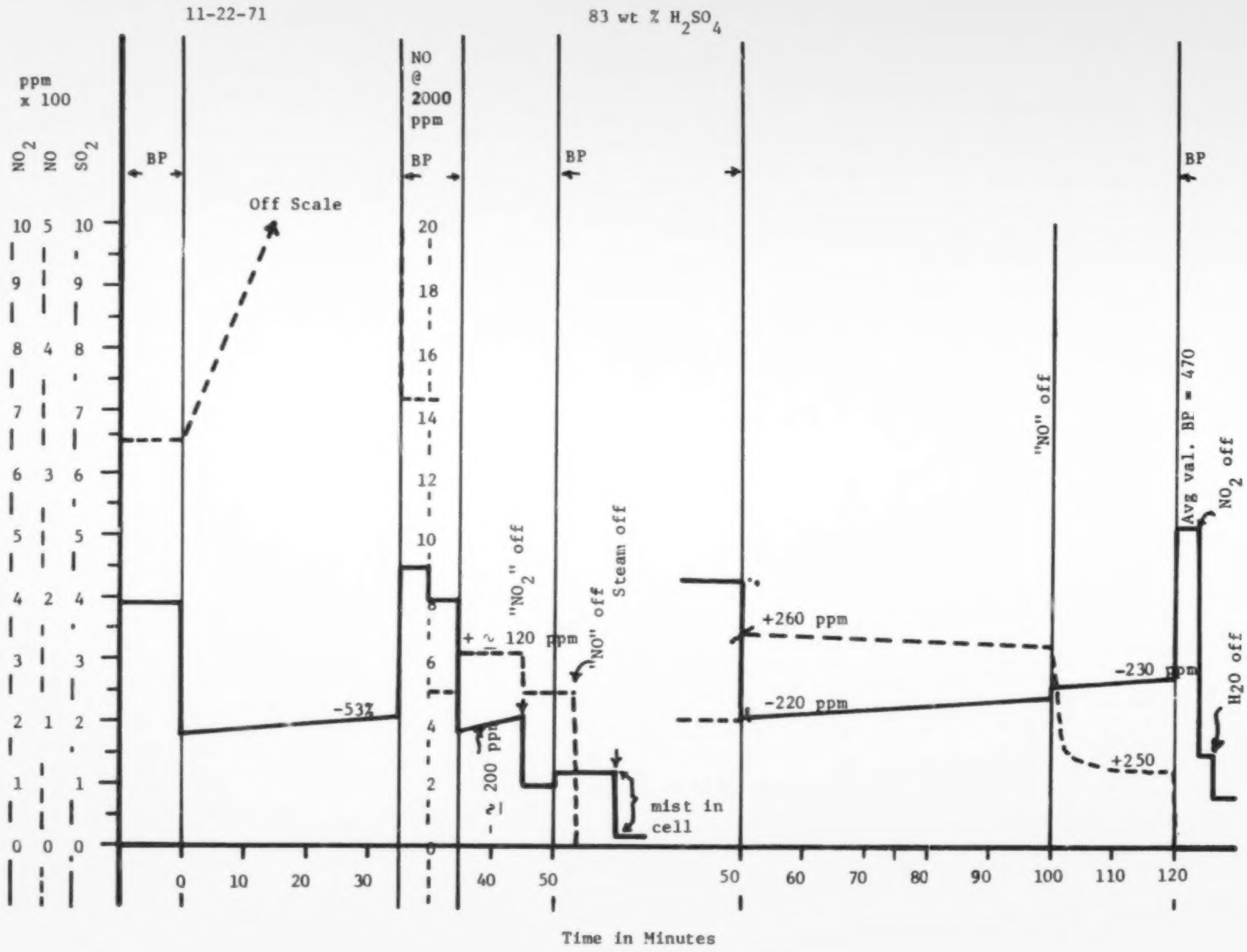
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F	Initial pH --	Final pH --
H_2O 10 %	CO_2 12 %	O_2 3 %
NO 338 ppm	NO_2 400 ppm	SO_2 -- ppm

COMMENT:

(1) The NO drop is nearly the same as the NO_2 which indicates that absorption is by N_2O_3 formation.

NO: Wet ice -> NDIR


11-22-71
83 wt % H_2SO_4
ppm
x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
Off Scale
NO
@
2000
ppm
20
18
16
14
12
10
8
6
4
2
0
-53%
+ ≈ 120 ppm
- ≈ 200 ppm
"NO_2" off
"NO" off
Steam off
mist in
cell
+260 ppm
-220 ppm
"NO" off
-230 ppm
+250
Avg val. BP = 470
NO_2 off
H_2O off
0
10
20
30
40
50
50
60
70
80
90
100
110
120
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 11-22-71 SCRUB: $83^{wt}\%$ H_2SO_4

OBJECT: NOX Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	275 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	325 ppm	NO_2	390 ppm	SO_2	-- ppm

COMMENT:

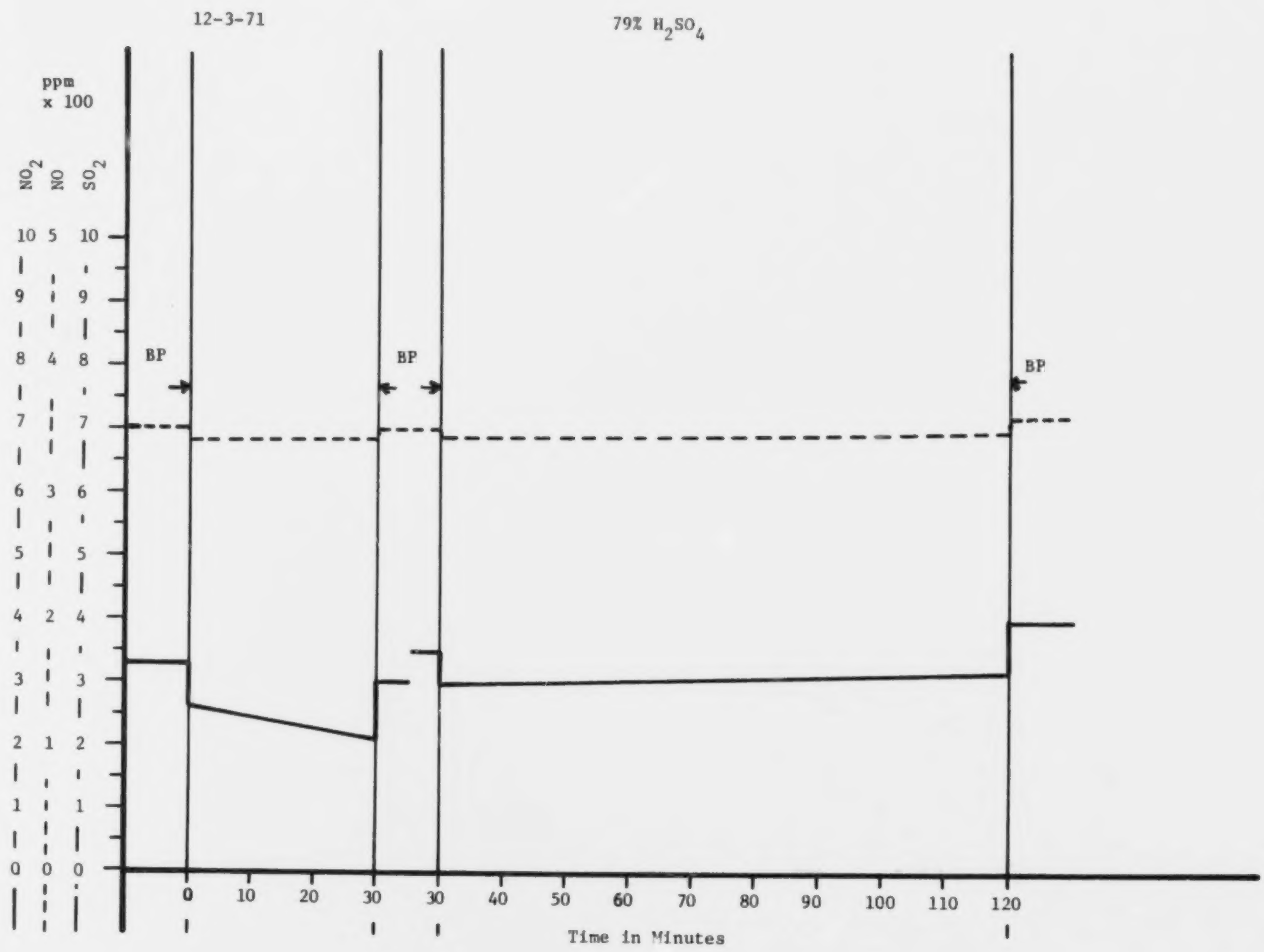
(1) The first attempt to run ended in failure. The thermocouple dissolved causing all sorts of errors. The system was rerun 12-3-71 with temp. control in an aux. oil bath and a glass thermometer in the H_2SO_4.

(2) The H_2SO_4 was contaminated with Fe-Ni-Cr from the SS304 of the thermocouple.

(3) Mist apparently forming in Dupont Cell; cell temperature 65°C.

(4) Data suspect due to (3).

NO: Wet ice -> NDIR


12-3-71
79% H_2SO_4
ppm
x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
BP
BP
0
10
20
30
30
40
50
60
70
80
90
100
110
120
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-3-71 SCRUB: 79wt% H_2SO_4

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 202 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

NO 325 ppm NO_2 330 ppm SO_2 -- ppm

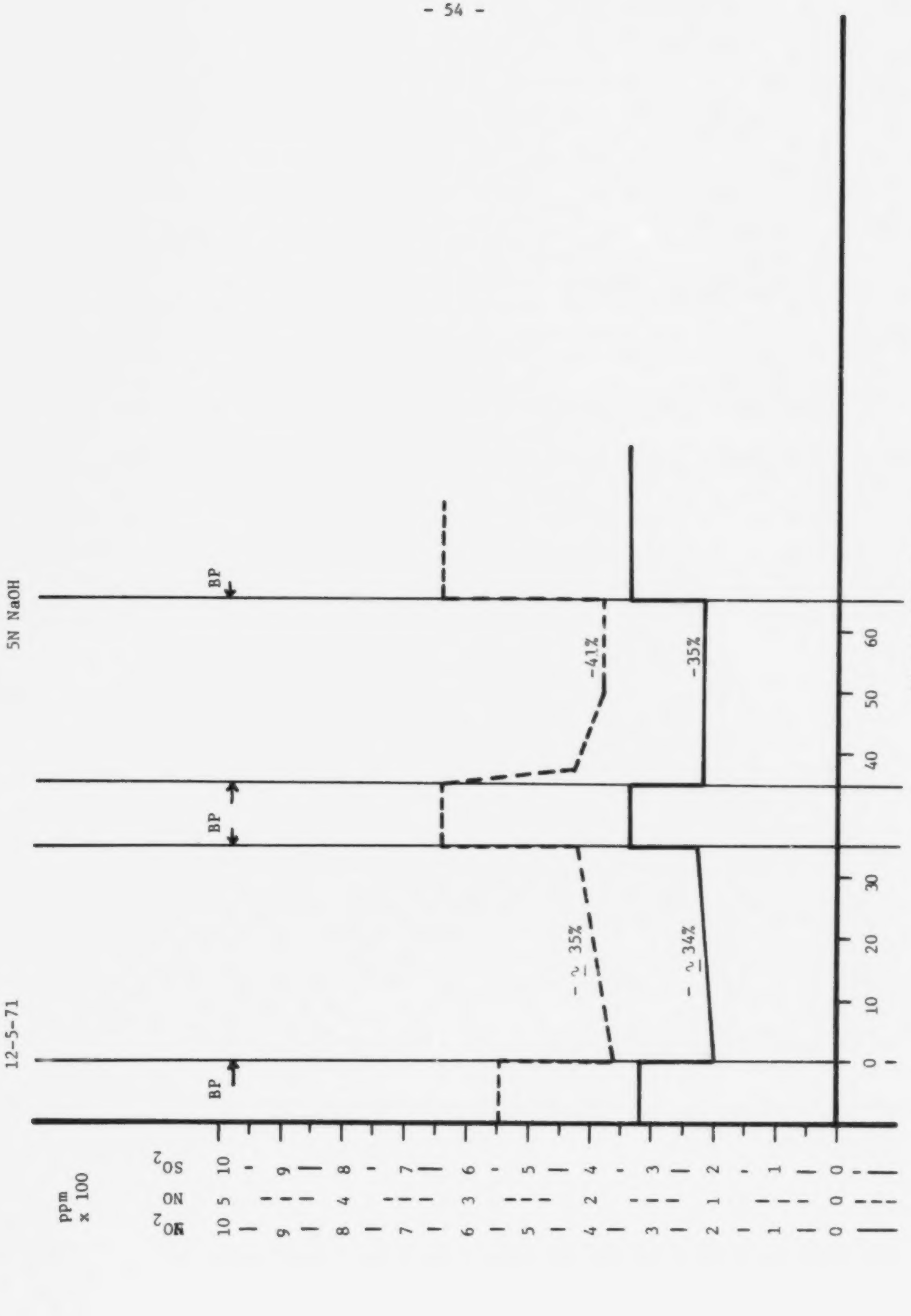
COMMENT:

(1) NO_2 absorption was **small**, ≈22%, the same as for water.

(2) NO was essentially unchanged with a max absorption of ≈ 2.5%.

(3) **First** 30 min NO_2 meter unstable.

NO: Dry ice -> NDIR


ppm
x 100
NO2
NO
SO2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
12-5-71
BP
BP
BP
5N NaOH
- ≈ 35%
- ≈ 34%
-41%
-35%
0
10
20
30
40
50
60
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-5-71

SCRUB: 5N NaOH

OBJECT: Sodium Hydroxide comparison to $(NH_4)_2SO_3$

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 112 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

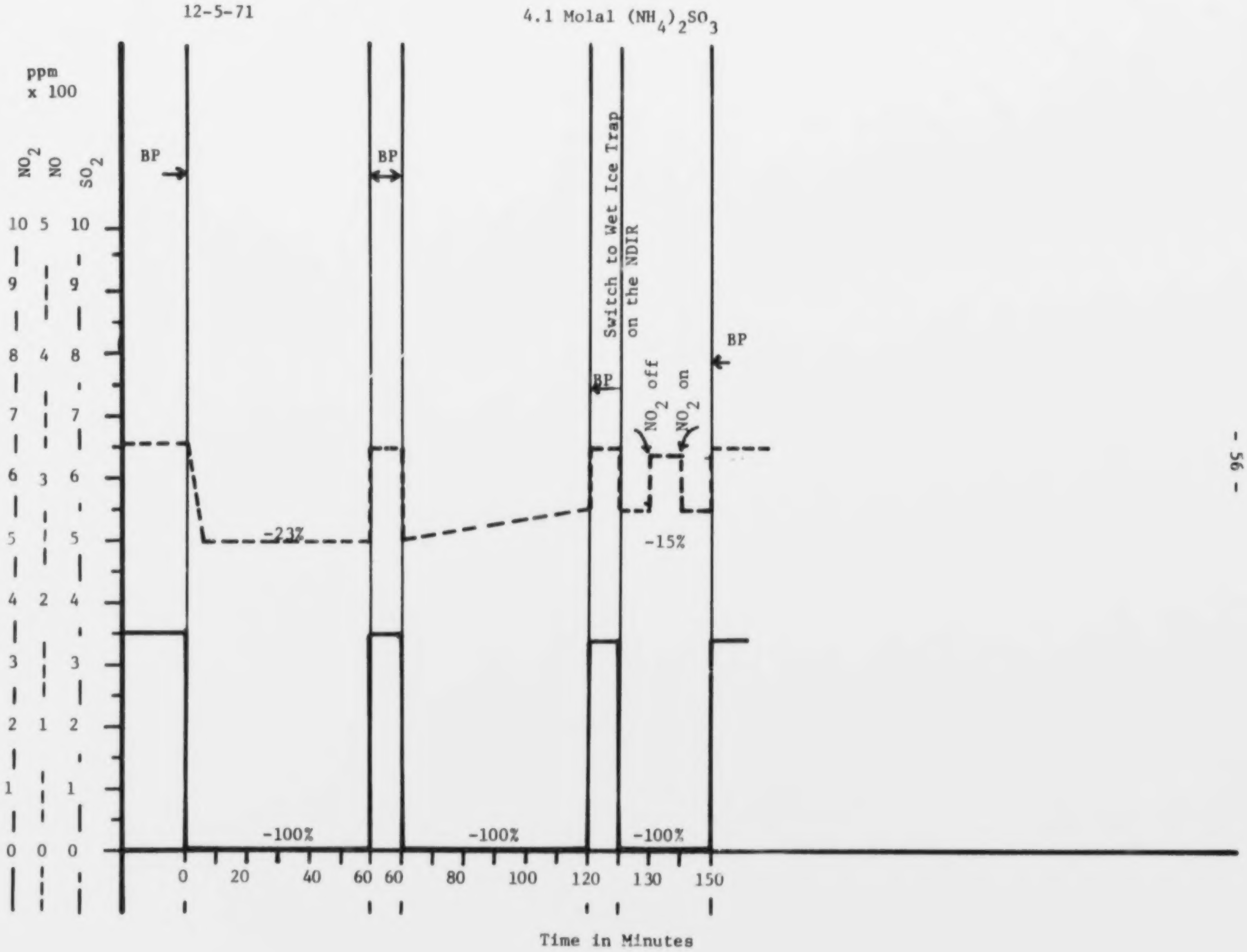
NO 274 ppm NO_2 320 ppm SO_2 -- ppm

COMMENT:

(1) NO & NO_2 scrubbing was in the 35% area with the NO increasing to about 41%.

(2) The NO_2 pullout was 120 ppm out of 340 & the NO 130 ppm out of 320.

NO: Dry Ice -> NDIR


12-5-71
4.1 Molal $(NH_4)_2SO_3$
ppm x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
BP
Switch to Wet Ice Trap on the NDIR
BP
NO_2 off
NO_2 on
BP
-23%
-15%
-100%
-100%
-100%
0
20
40
60
60
80
100
120
130
150
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-5-71

SCRUB: 4.1 Molal $(NH_4)_2SO_3$

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 112 °F

Initial pH --

Final pH --

H_2O 10 %

CO_2 12 %

O_2 3 %

NO 328 ppm

NO_2 350 ppm

SO_2 -- ppm

COMMENT:

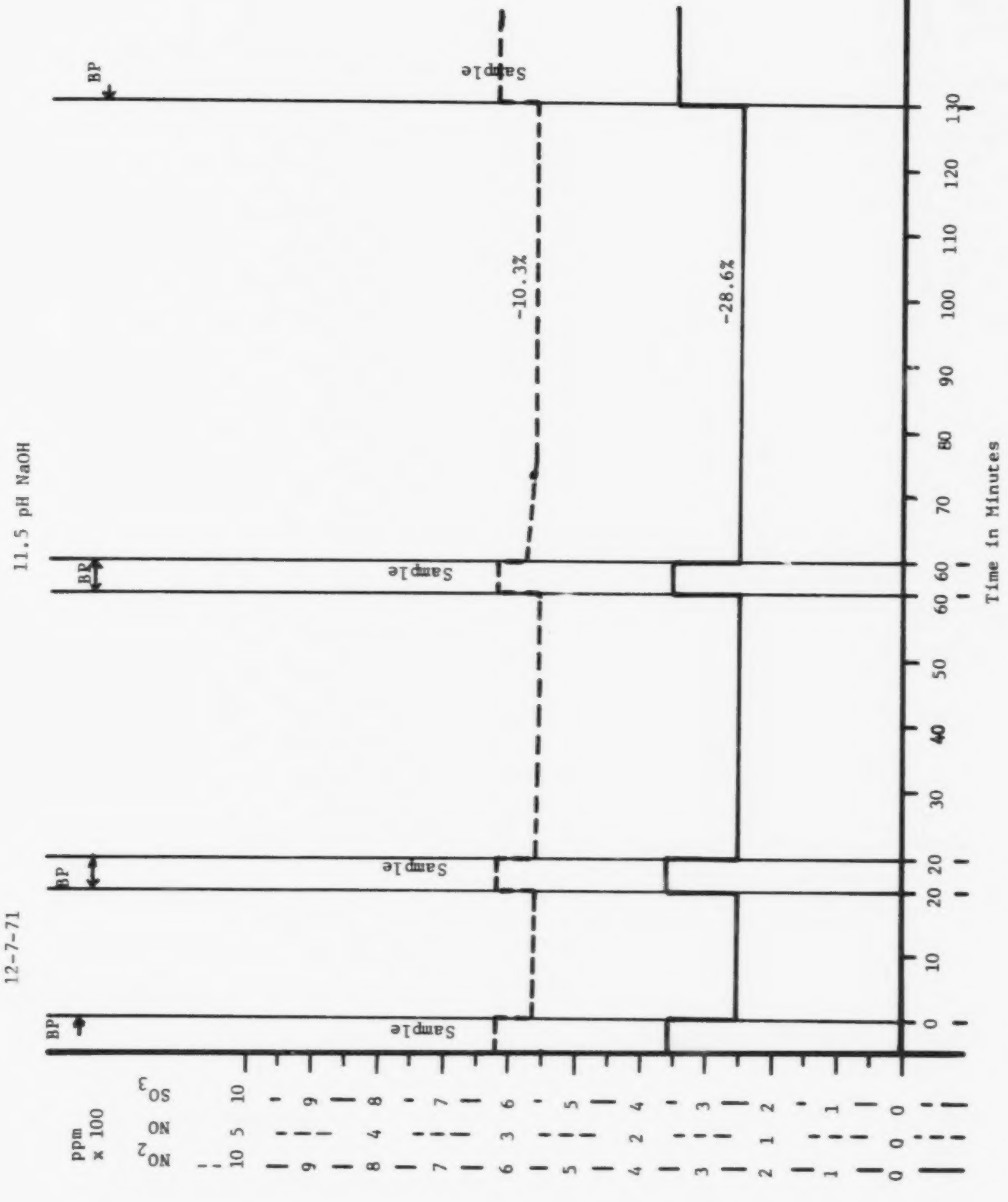
(1) NO_2 scrubbing is 100%.

(2) NO absorption starts @ 2.3% & drops 15% over _ 2 hrs.

(3) With NO_2 turned off, no NO is absorbed.

(4) After 140 minutes on line solution analysis by UV showed 5.2 millimoles of NO_3^- and 0.6 millimoles of NO_2^-.

NO: Dry ice trap -> NDIR


12-7-71
11.5 pH NaOH
BP
BP
BP
BP
Sample
Sample
Sample
Sample
-10.3%
-28.6%
ppm x 100
NO_2
NO
SO_3
0
10
20
20
30
40
50
60
60
70
80
90
100
110
120
130
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-7-71 SCRUB: NaOH @ 11.5 (3.16×10^{-3} molar)

same as sat'd $Ca(OH)_2$

OBJECT: Compare hydroxide scrubbing at same pH

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

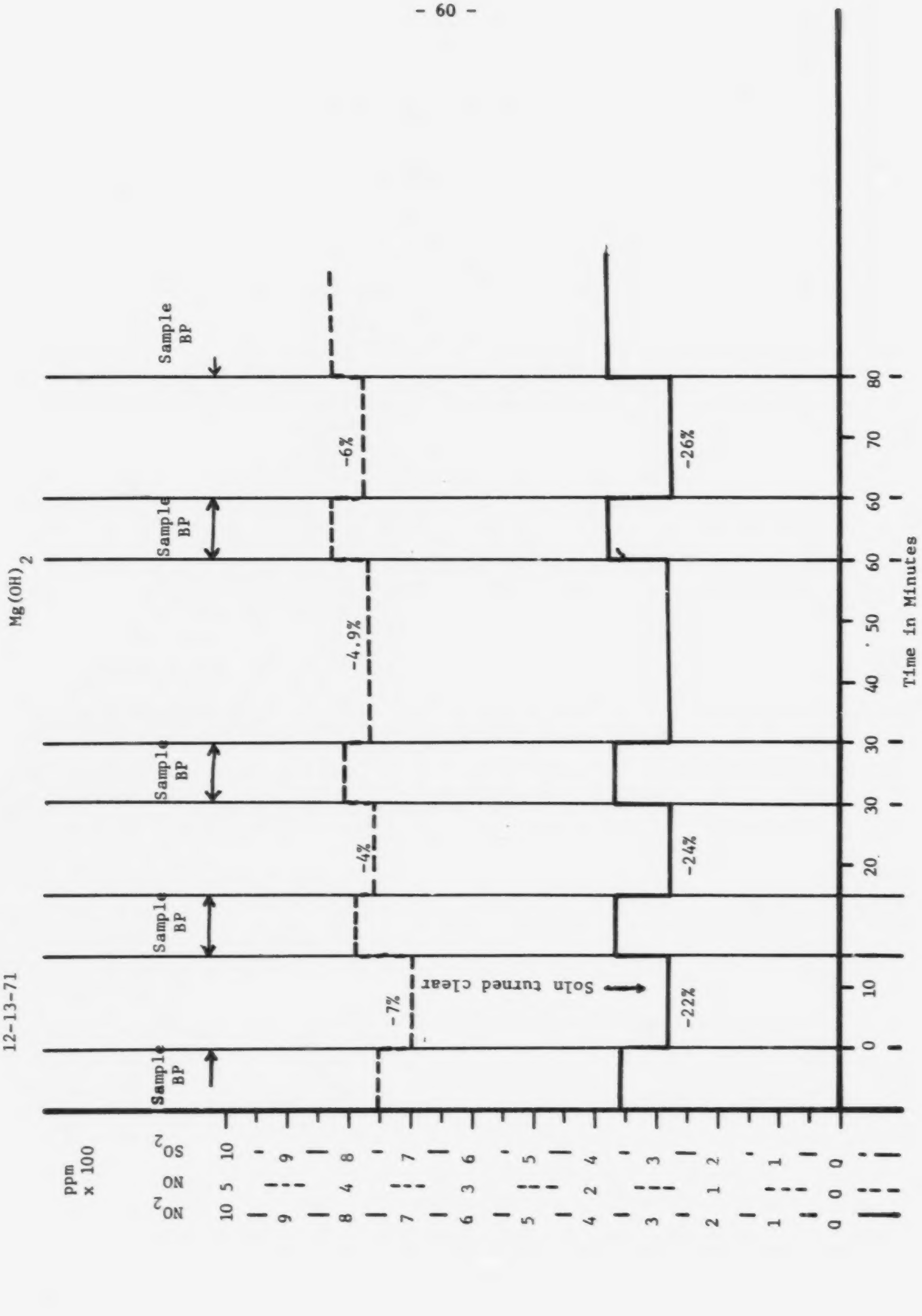
Pot Temp.	120 °F	Initial pH	11.5	Final pH	6.3
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	311 ppm	NO_2	360 ppm	SO_2	-- ppm

COMMENT:

(1) Δ NO ≈ -10%

Δ NO_2 ≈ -79%

NO: Wet ice trap -> NDIR


12-13-71
Mg(OH)$_2$
Sample BP
Sample BP
Sample BP
Sample BP
Sample BP
-7%
-4%
-4.9%
-6%
-22%
-24%
-26%
Soln turned clear
ppm x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
0
10
20
30
30
40
50
60
60
70
80
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-13-71

SCRUB: Sat'd soln. with slight excess of $Mg(OH)_2$

OBJECT: NOX Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 8.9 Final pH 7.5

H_2O 10 % CO_2 12 % O_2 3 %

NO 377 ppm NO_2 360 ppm SO_2 -- ppm

COMMENT:

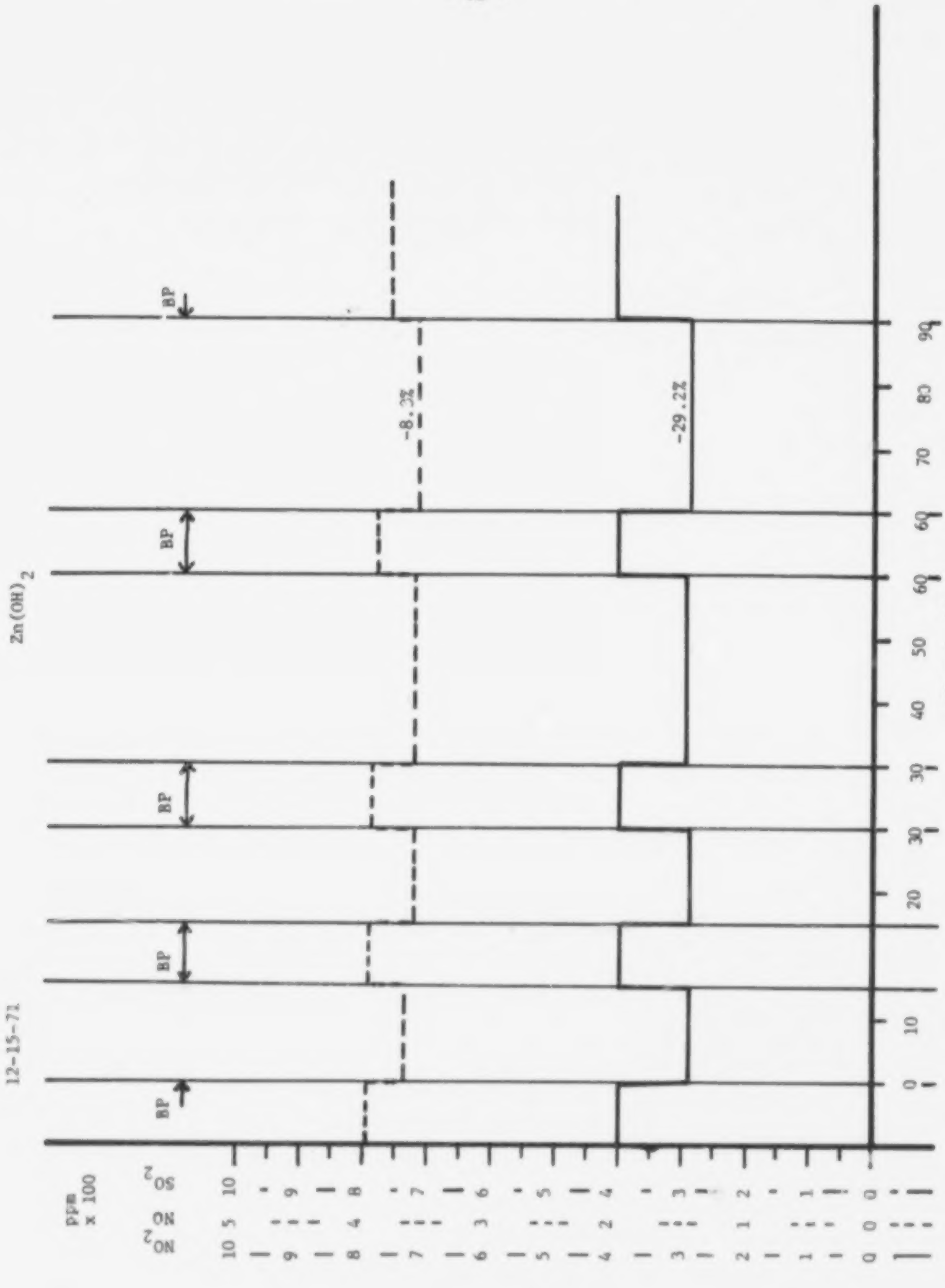
(1) NO pullout was ≈ 5%

(2) NO_2 pullout was ≈ 25%

(3) Scrub. turned from cloudy to clear after 10 minutes.

(4) After 80 minutes on line, solution analysis (spectrophotometric) gave zero nitrate and 0.9×10^{-3} M nitrate.

NO: Sat'd Na_2SO_3 in HOAc -> dry ice -> NDIR


12-15-71
$Zn(OH)_2$
BP
BP
BP
BP
BP
-8.3%
-29.2%
ppm x 100
NO_2
NO
SO_2
10 9 8 7 6 5 4 3 2 1 0
10 5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
0 10 20 30 30 40 50 60 60 70 80 90
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-15-71

SCRUB: Sat'd soln. of $Zn(OH)_2$

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 119 °F Initial pH 7.5 Final pH 6.9

H_2O 10 % CO_2 12 % O_2 3 %

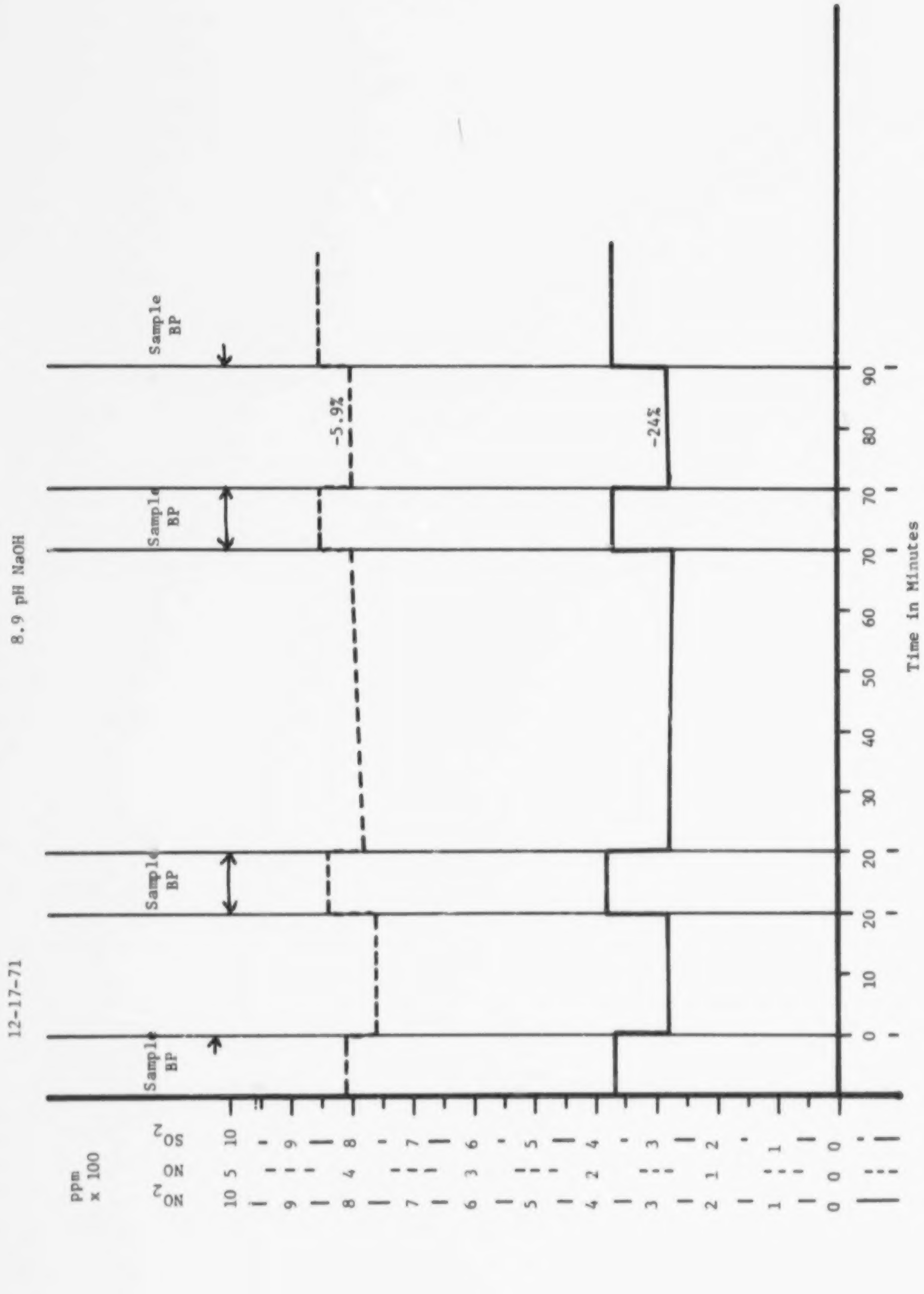
NO 397 ppm NO_2 400 ppm SO_2 -- ppm

COMMENT:

(1) Δ NO = 8.3%
Δ NO_2 = 29%

(2) After 90 minutes on line, spectrophotometric solution analysis gave 0.3×10^{-3} M nitrate and 1.4×10^{-3} nitrite.

NO: HOAc · Na_2SO_3 -> dry ice ->NDIR


12-17-71
8.9 pH NaOH
ppm
x 100
NO2 NO SO2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
Sample BP
Sample BP
Sample BP
Sample BP
-5.9%
-24%
0
10
20
20
30
40
50
60
70
70
80
90
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-17-71

SCRUB: NaOH @ pH8.9, same as sat'd $Mg(OH)_2$

OBJECT: Compare hydroxide scrubbing at same pH

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 120 °F Initial pH 8.9 Final pH ________

H_2O 10 % CO_2 12 % O_2 3 %

NO 404 ppm NO_2 370 ppm SO_2 -- ppm

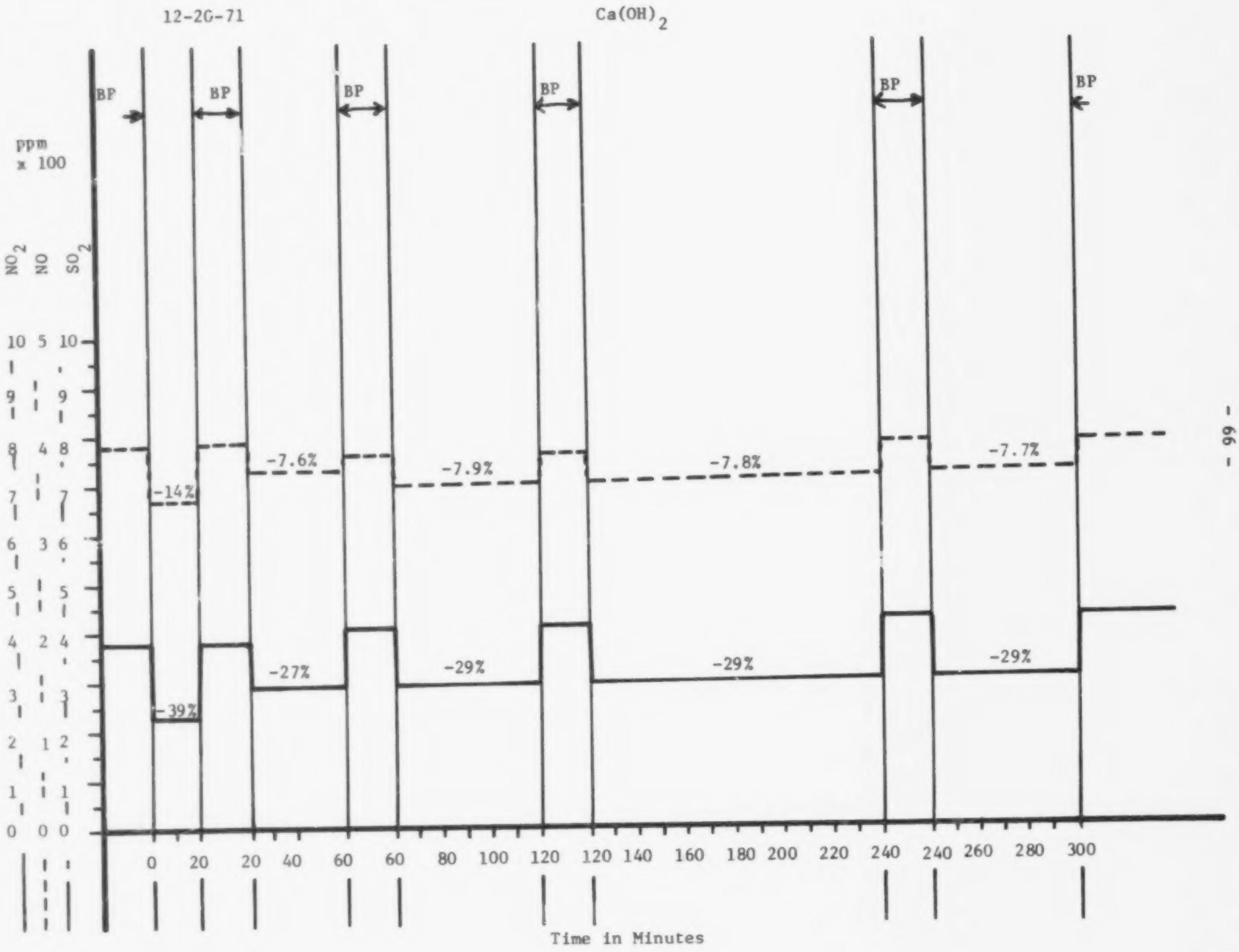
COMMENT:

(1) Δ NO ≈ 6%
Δ NO_2 ≈ 24%

(2) pH dropped 4 after 70 minutes on line.

(3) After 70 minutes on line, spectrophotometric analysis of solution gave 0.3×10^{-3} M nitrate and 1.3×10^{-3} M nitrite.

NO: Na_2SO_3 in HOAc -> dry ice trap -> NDIR


12-2C-71
Ca(OH)$_2$
ppm
x 100
NO$_2$
NO
SO$_2$
BP
BP
BP
BP
BP
BP
-14%
-7.6%
-7.9%
-7.8%
-7.7%
-39%
-27%
-29%
-29%
-29%
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
0
20
20
40
60
60
80
100
120
120
140
160
180
200
220
240
240
260
280
300
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 12-20-71 SCRUB: Sat'd soln. $Ca(OH)_2$

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 121 °F Initial pH 11.5 Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

NO 390 ppm NO_2 380 ppm SO_2 -- ppm

COMMENT:

(1) @ 0 → 20 min.	Δ NO = 14%	ΔNO_2 = 39%
20 → 60	7.6	27
60 → 120	7.9	29
120 → 240	7.8	29
240 → 300	7.7	29

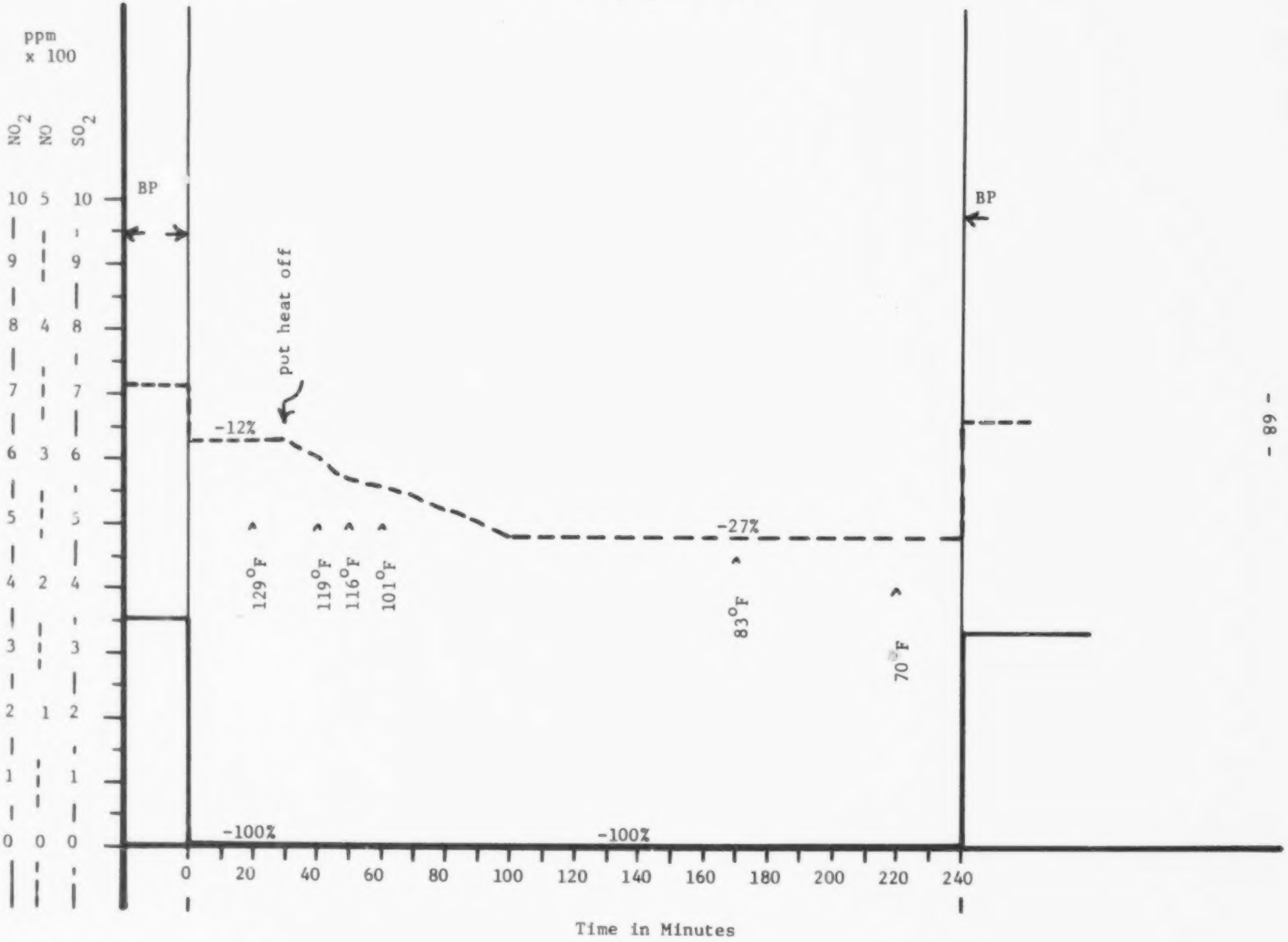
(2) During first 100 minutes pH dropped from 11.5 to 7.5

(3) After 300 minutes on line, spectrophotometric solution analysis gave 0.4×10^{-3} M nitrate and 4.6×10^{-3} M nitrite.

NO: HOAc · Na_2SO_3 -> dry ice trap -> NDIR

12-21-71

Sat'd Na_2SO_3 in 5N NaOH



NOX SCRUBBING DATA SHEET

DATE: 12-21-71

SCRUB: A saturated soln. of Na_2SO_3 in 5N NaOH

OBJECT: Study Scrubbing by Strongly Basic Na_2SO_3

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. Varies °F Initial pH ______ Final pH ______

H_2O 10 % CO_2 12 % O_2 3 %

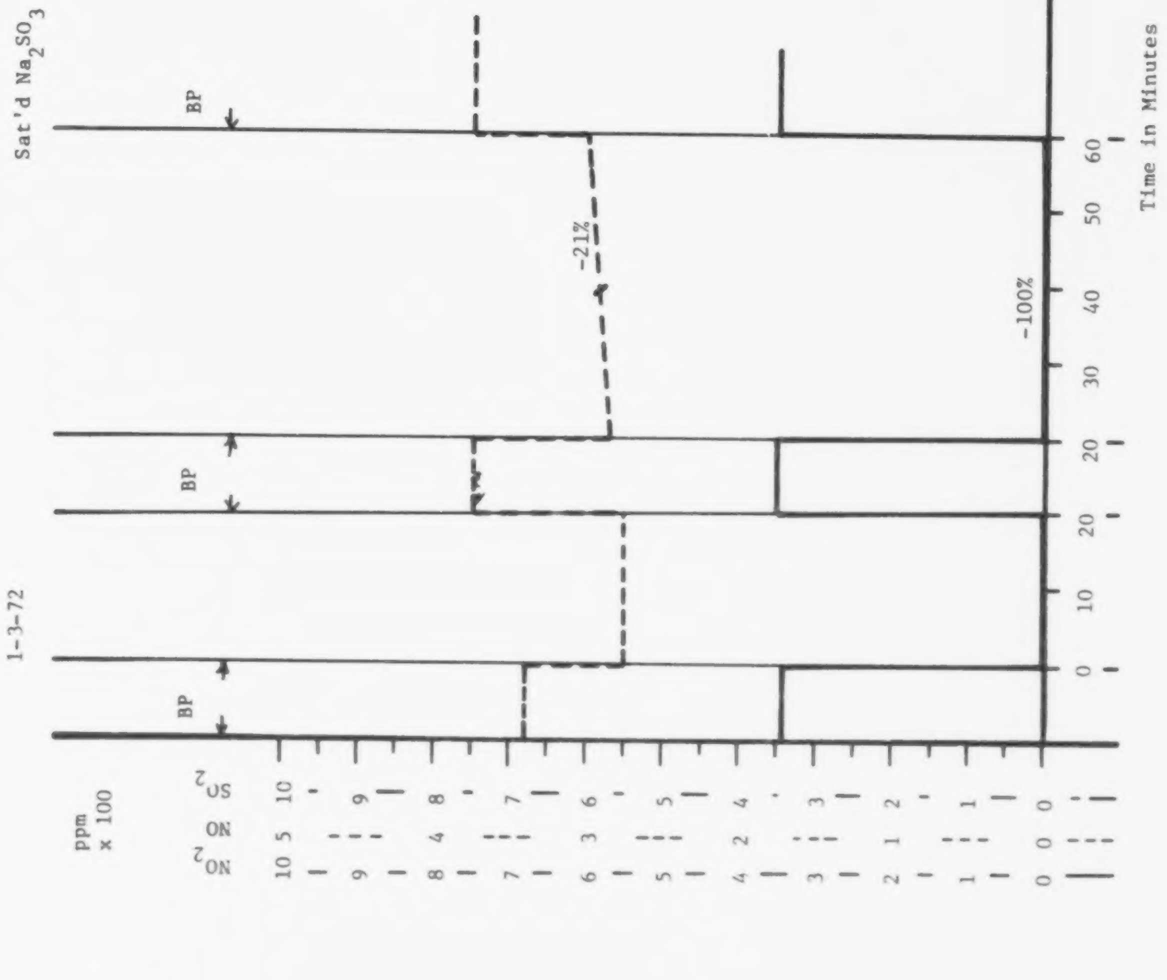
NO 357 ppm NO_2 355 ppm SO_2 -- ppm

COMMENT:

(1) At the higher temperature (129°F) the NO removal was 12%; NO_2 removal was 100%.

(2) As the temperature went down, the NO pullout increased to 27% @ ≈ 80°F.

NO: HOAc · Na_2SO_3 -> dry ice ->NDIR


1-3-72
Sat'd Na$_2$SO$_3$
BP
BP
BP
-21%
-100%
0
10
20
20
30
40
50
60
Time in Minutes
ppm x 100
NO$_2$
NO
SO$_2$
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 1-3-72 SCRUB: Sat'd sol'n Na_2SO_3

(approximately 2.3 → 2.5 molal)

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	122 °F	Initial pH	10	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	340 ppm	NO_2	340 ppm	SO_2	-- ppm

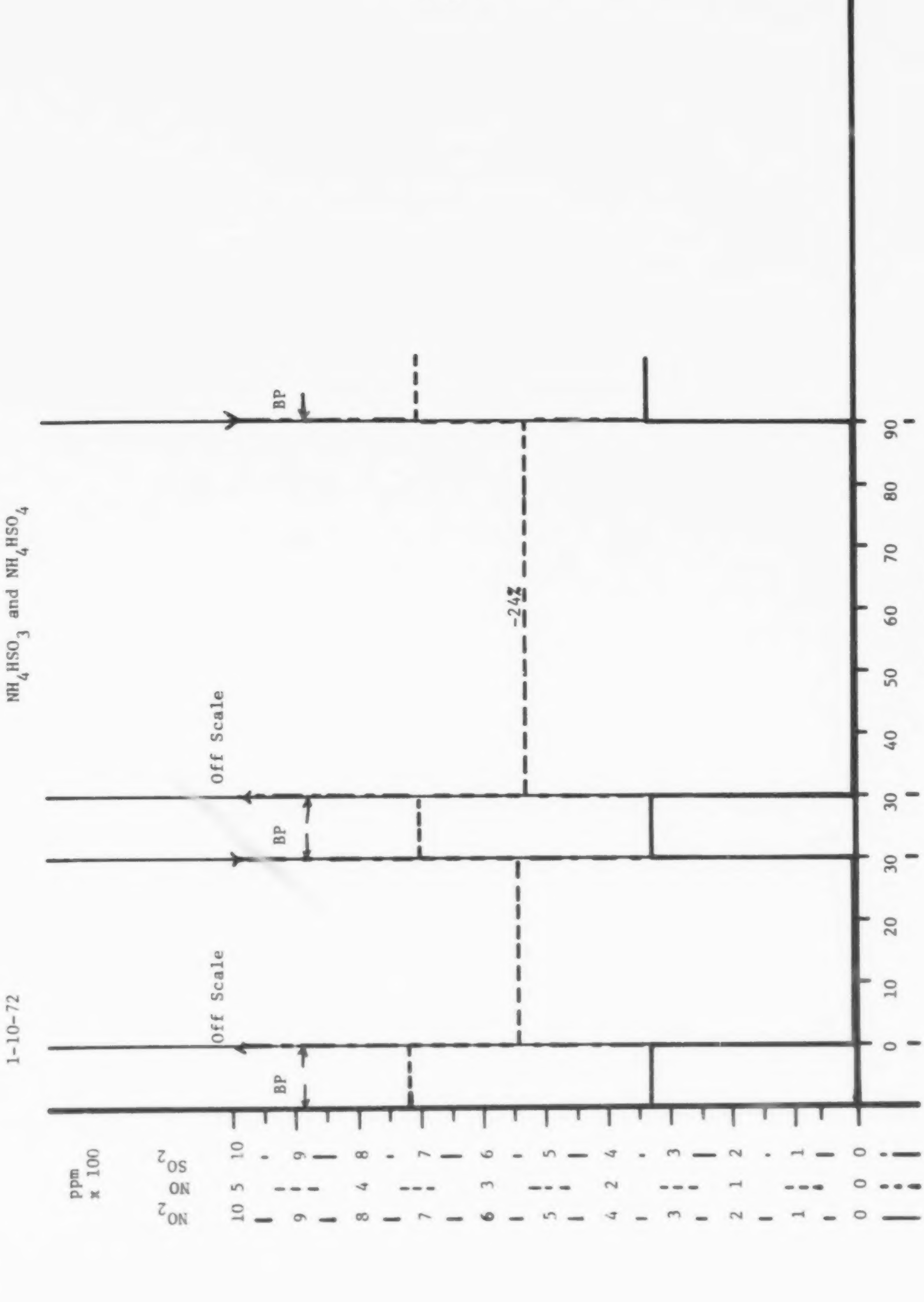
COMMENT:

(1) No SO_2 generated.

(2) Δ NO = 21% Δ NO_2 = 100%

(3) $Na_2SO_3 \cdot 7H_2O$ @ 196 gm/100ml (CRC handbook) = ≈ 3.5 molal in Na_2SO_3 @ 40°C. This is higher than observed.

NO: Na_2SO_3 -> dry ice -> NDIR


1-10-72
NH4HSO3 and NH4HSO4
Off Scale
Off Scale
BP
BP
BP
-24%
Time in Minutes
0
10
20
30
30
40
50
60
70
80
90
ppm
x 100
NO2
NO
SO2
10 10 5
9 9
8 8 4
7 7
6 6 3
5 5
4 4 2
3 3
2 2 1
1 1
0 0 0

NOX SCRUBBING DATA SHEET

DATE: 1-10-72 SCRUB: $NH_4HSO_3 + NH_4HSO_4$

3.60 molal NH_4HSO_3, 1.88 molal NH_4HSO_4

OBJECT: NOX Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 2.4 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

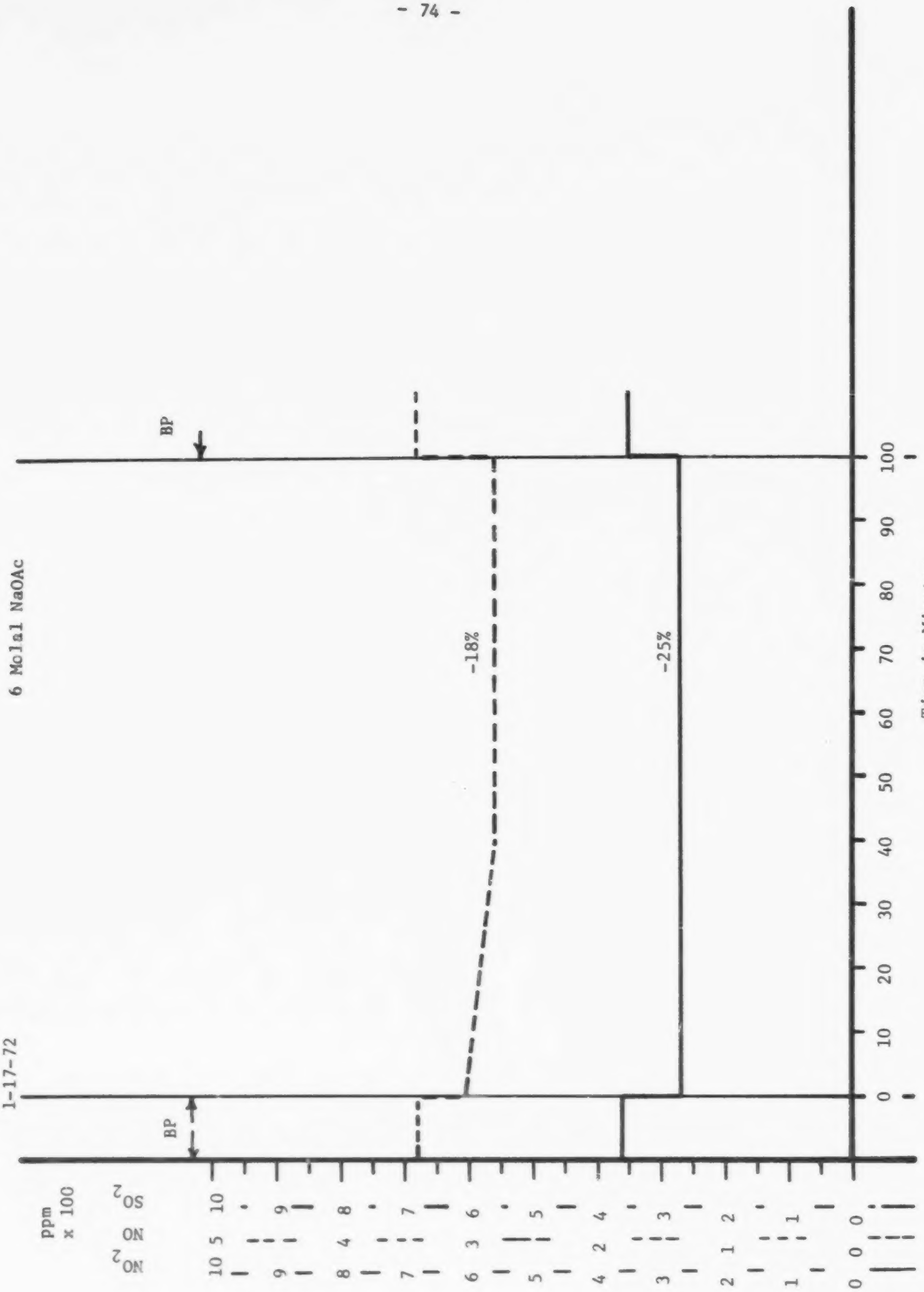
NO 360 ppm NO_2 330 ppm SO_2 0 ppm

COMMENT:

(1) Copies generation of SO_2 on mixing $[HSO_4^- + HSO_3^- \longrightarrow SO_4^{=} + H_2SO_3 \longrightarrow H_2O + SO_2]$.

(2) $\Delta NO_2 = 100\%$
$\Delta NO \simeq 24\%$
generated $SO_2 > 1000$ ppm

NO; Na_2SO_3 -> dry ice -> NDIR


6 Molal NaOAc
1-17-72
BP
BP
-18%
-25%
Time in Minutes
0
10
20
30
40
50
60
70
80
90
100
Ppm x 100
NO_2
NO
SO_2
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5
0 1 2 3 4 5 6 7 8 9 10

NOX SCRUBBING DATA SHEET

DATE: 1-17-72

SCRUB: 6 molal NaOAc

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 119 °F

Initial pH --

Final pH --

H_2O 10 %

CO_2 12 %

O_2 3 %

NO 340 ppm

NO_2 360 ppm

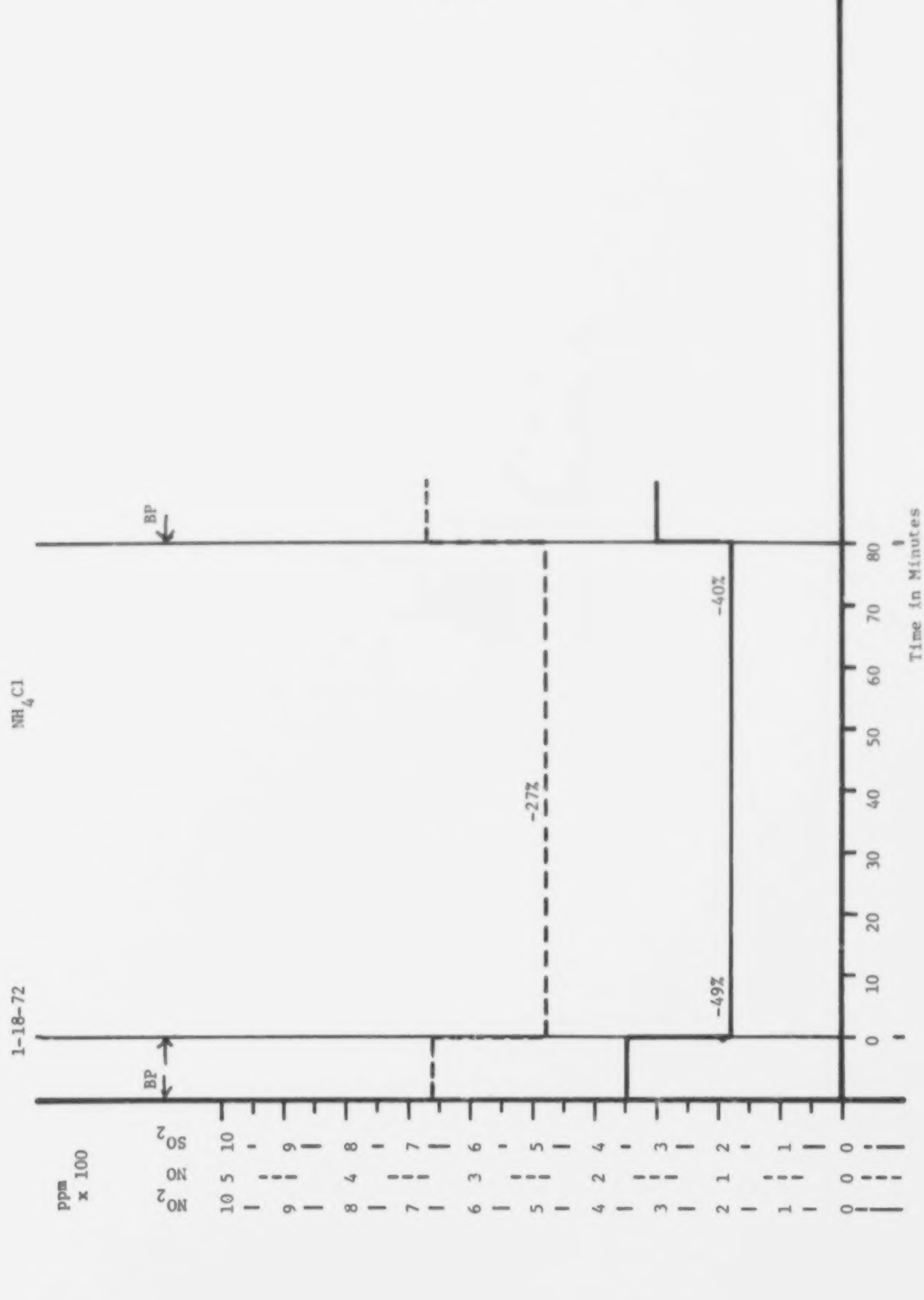
SO_2 ppm

COMMENT:

Δ NO = 18%

Δ NO_2 = 25%

NO: Dry ice -> NDIR


ppm
x 100
NO2
NO
SO2
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0
BP
1-18-72
NH4Cl
BP
-27%
-49%
-40%
0 10 20 30 40 50 60 70 80
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 1-18-72 SCRUB: 8.4 m NH_4 Cl

OBJECT: Absorb NOX

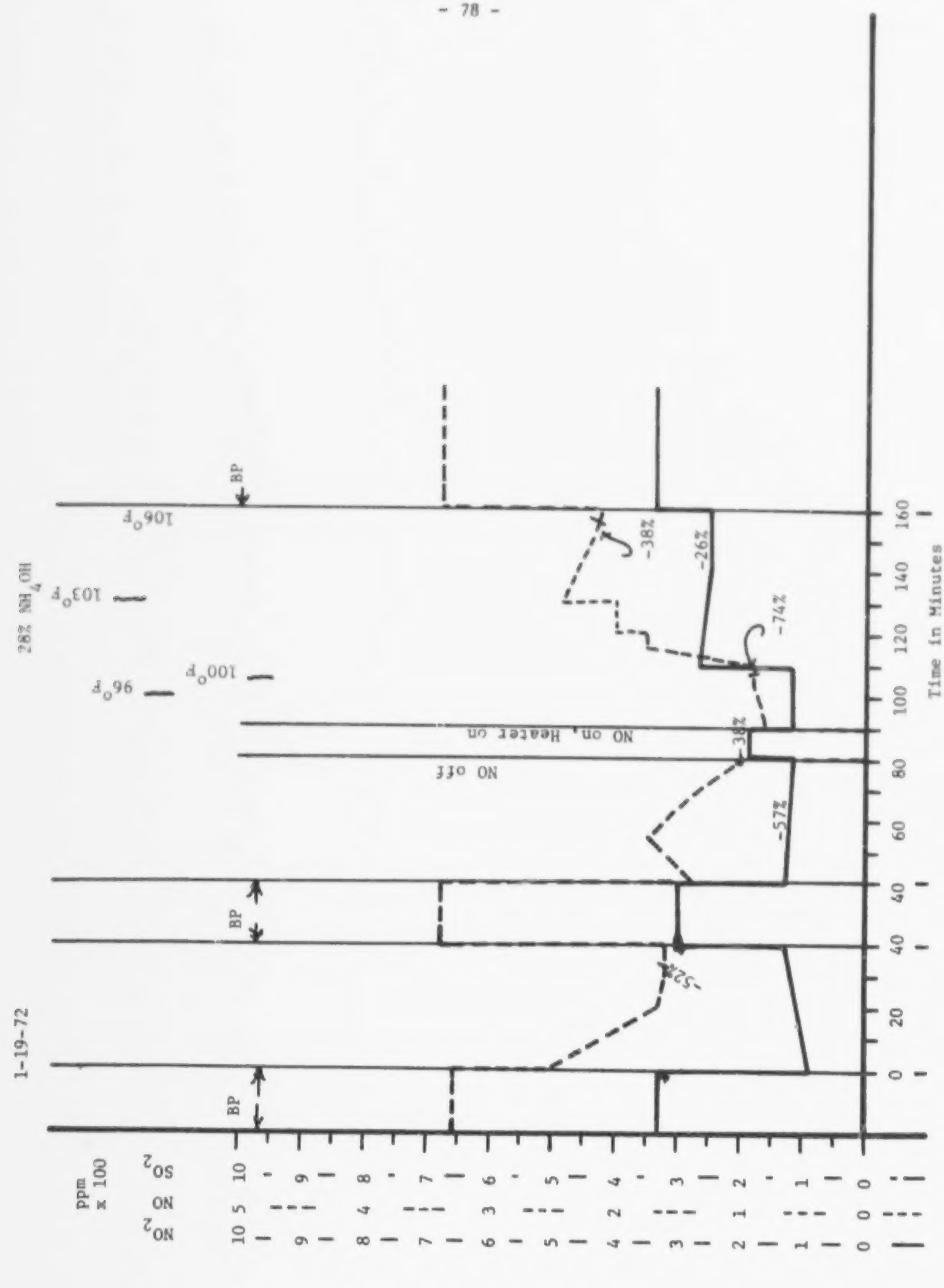
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	123 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	330 ppm	NO_2	350 ppm	SO_2	ppm

COMMENT:

(1) Δ NO ≈ 27%
Δ NO ≈ 49 -> 40%

NO: Dry ice -> NDIR (≈ 23% conv. NO_2 -> NO)


1-19-72
BP
BP
BP
28% NH_4OH
96°F
100°F
103°F
106°F
NO off
NO on, Heater on
-52%
-57%
-38%
-74%
-38%
-26%
Time in Minutes
0
20
40
40
60
80
100
120
140
160
ppm x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0

NOX SCRUBBING DATA SHEET

DATE: 1-19-72 SCRUB: 28 wt. % NH_4OH

OBJECT: Ammonia Scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	75 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	328 ppm	NO_2	330 ppm	SO_2	ppm

COMMENT:

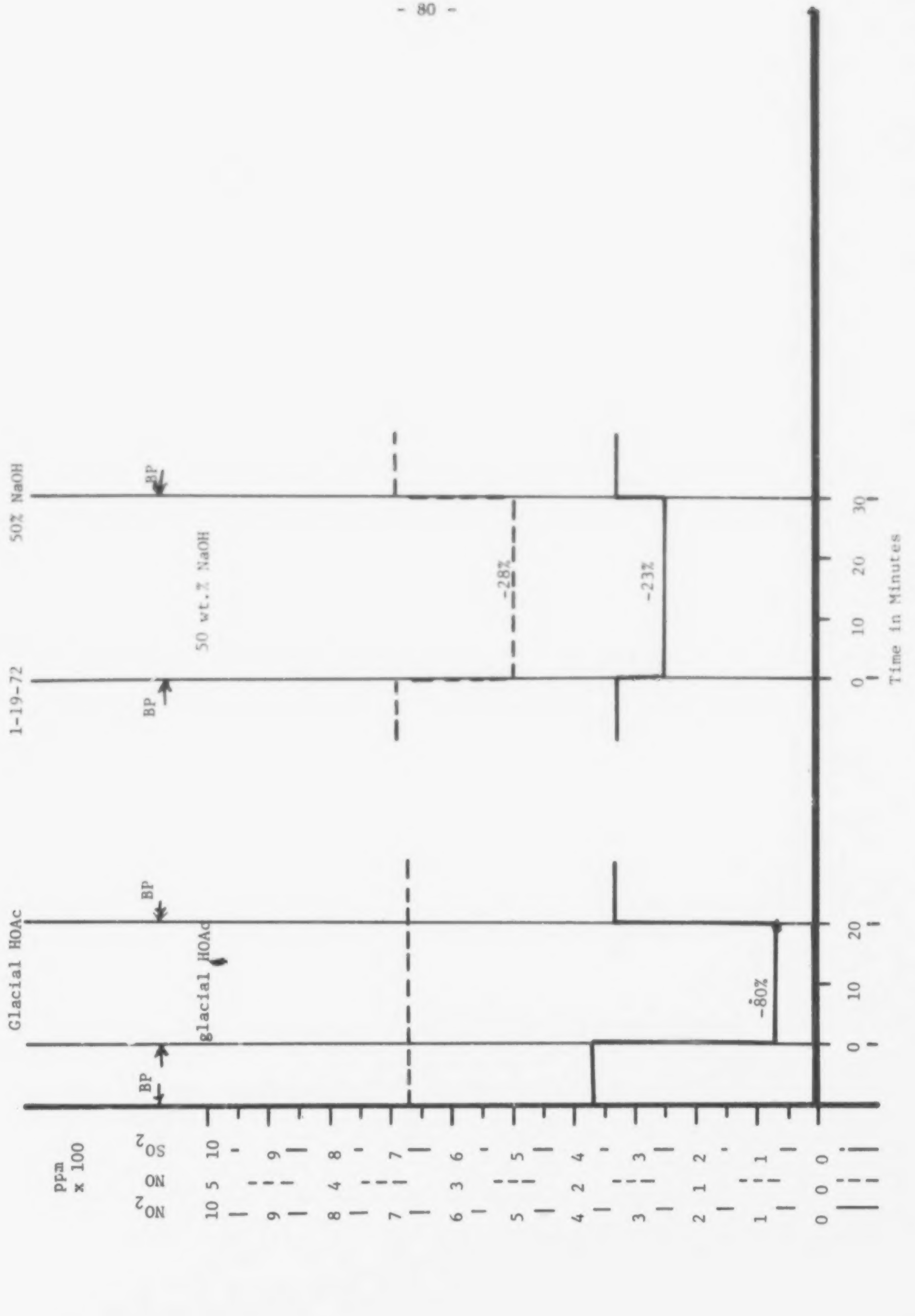
(1) An H_2SO_4 trap was used to protect the NDIR from NH_3. The trap was allowed to equilibrate with NO-NO_2. On by-pass without the H_2SO_4, the NDIR read 83, with H_2SO_4, 82 1/2. The NO_2 was unchanged.

(2) Best pullout was @ rm. temp. and was 57% NO_2, 74% NO.

(3) At elevated temperature (106°F) NO_x absorption was 38% NO, 26% NO_2.

(4) NH_3 boil off is a severe problem.

NO: *See comment (1)* -> H_2SO_4 -> dry ice trap -> NDIR
(≈ 23% of NO_2 conv. -> NO)


ppm
x 100
NO2
NO
SO2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
BP
Glacial HOAc
glacial HOAc
BP
-80%
0
10
20
1-19-72
BP
50 wt.% NaOH
50% NaOH
BP
-28%
-23%
0
10
20
30
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 1-19-72 SCRUB: HOAc glacial

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	120 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	335 ppm	NO_2	370 ppm	SO_2	-- ppm

COMMENT:

(1) NO level not effected
NO_2 = 80%

NO: Dry ice -> NDIR

NOX SCRUBBING DATA SHEET

DATE: 1-19-72

SCRUB: 50 wt. % NaOH

OBJECT: Absorb NOX

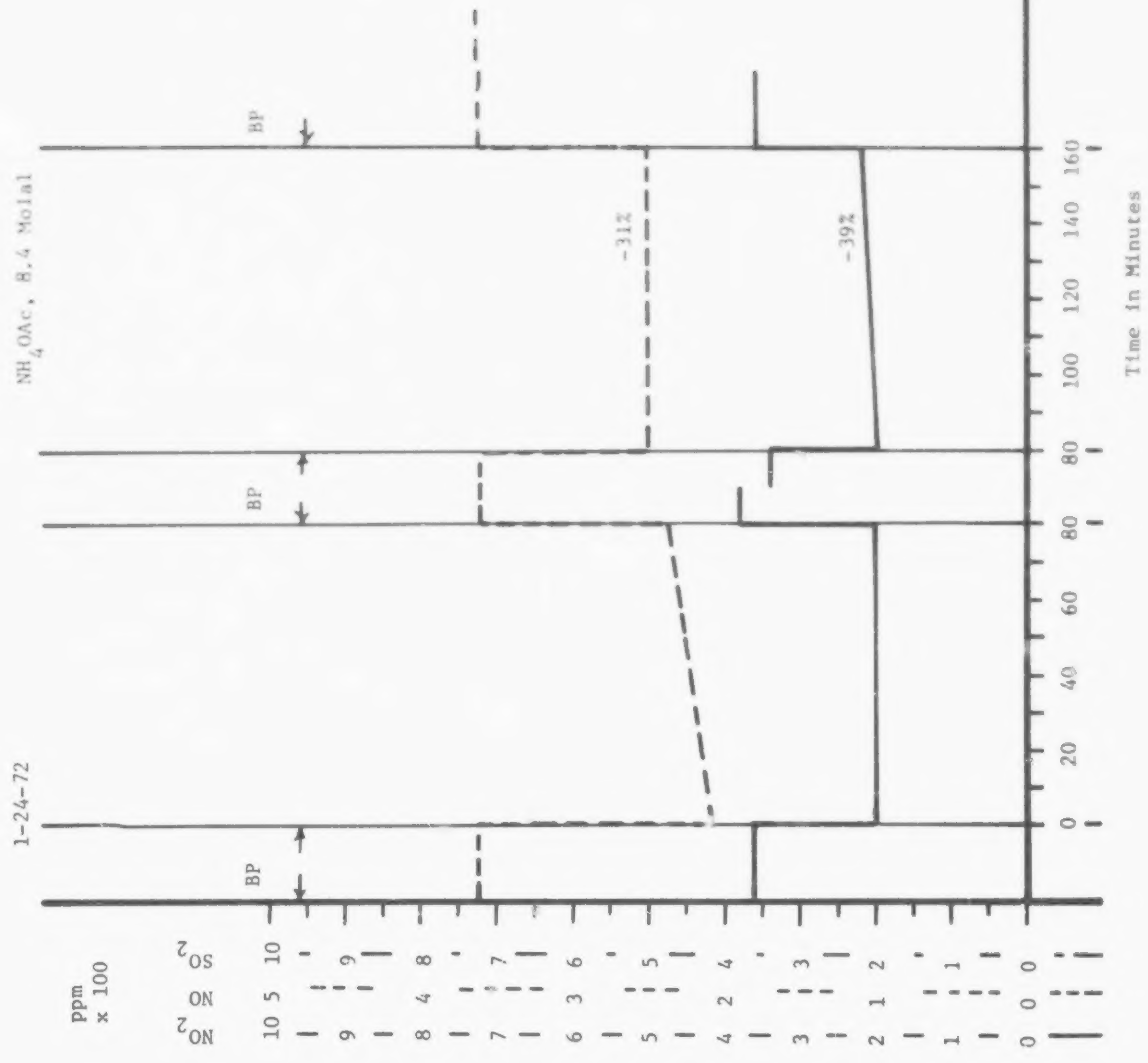
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	120 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	345 ppm	NO_2	330 ppm	SO_2	-- ppm

COMMENT:

(1) Δ NO_2 = 23%
Δ NO = 28%

NO: Dry ice -> NDIR


ppm
x 100
NO$_2$
NO
SO$_2$
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
BP
BP
1-24-72
NH$_4$OAc, 8.4 Molal
-31%
-39%
0
20
40
60
80
80
100
120
140
160
160
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 1-24-72 SCRUB: 8.4 Molal NH_4 OAc

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 120 °F Initial pH - Final pH -

H_2O 10 % CO_2 12 % O_2 3 %

NO 362 ppm NO_2 360 ppm SO_2 - ppm

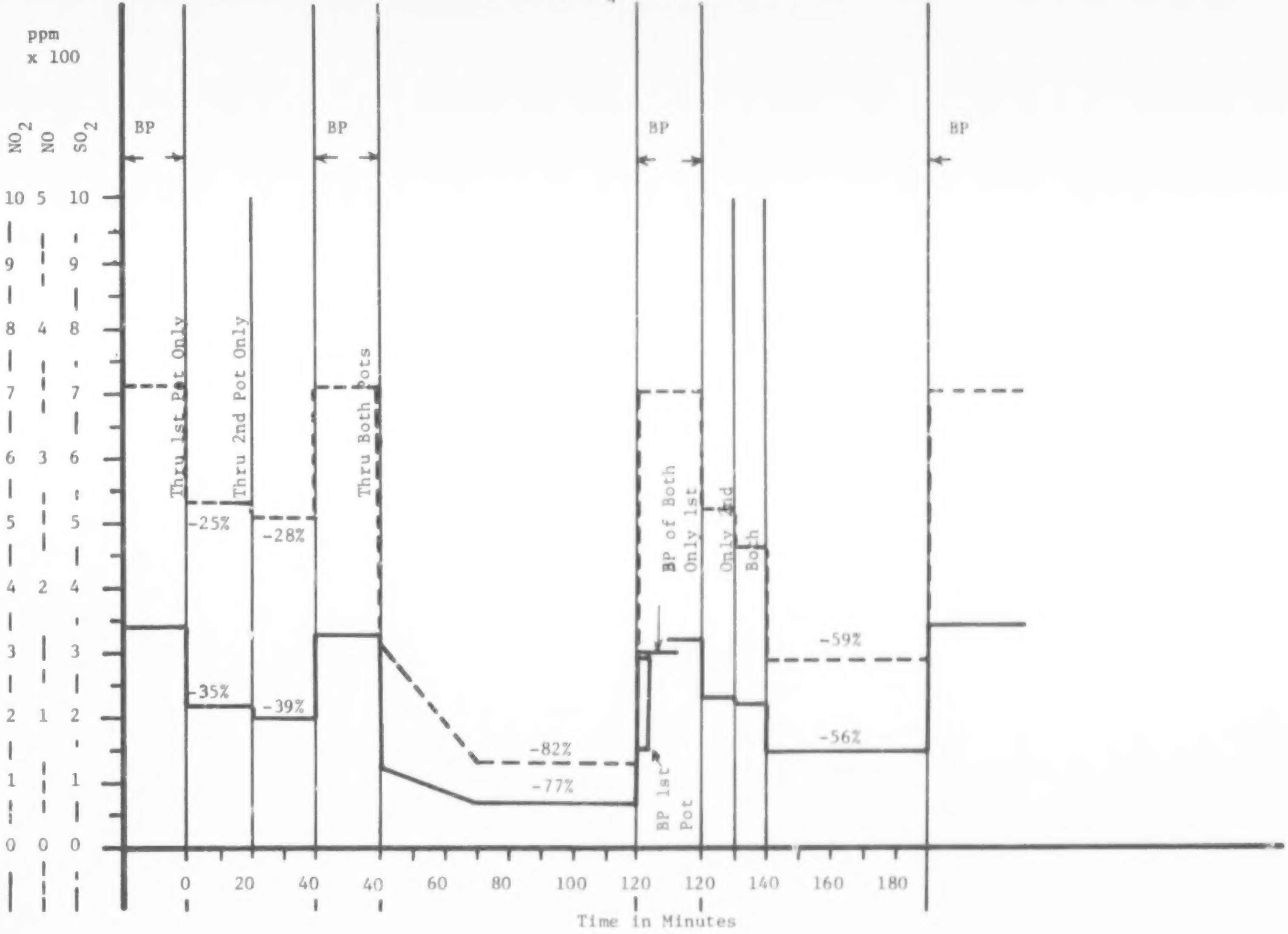
COMMENT:

(1) Δ NO ≈ 31% Δ NO_2 ≈ 39%

NO: H_2SO_4 (sat'd with NO & NO_2) ⟶ dry ice ⟶ NDIR

1-25-72

7.0 Molal NH_4OAc, Dual Series Pots



NOX SCRUBBING DATA SHEET

DATE: 1-25-72 SCRUB: 7.0 Molal NH_4OAc Two Baths

OBJECT: Double Bath Run

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	123 °F	Initial pH		Final pH	
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	354 ppm	NO_2	340 ppm	SO_2	- ppm

COMMENT:

(1) Two pots arranged in series sequence.

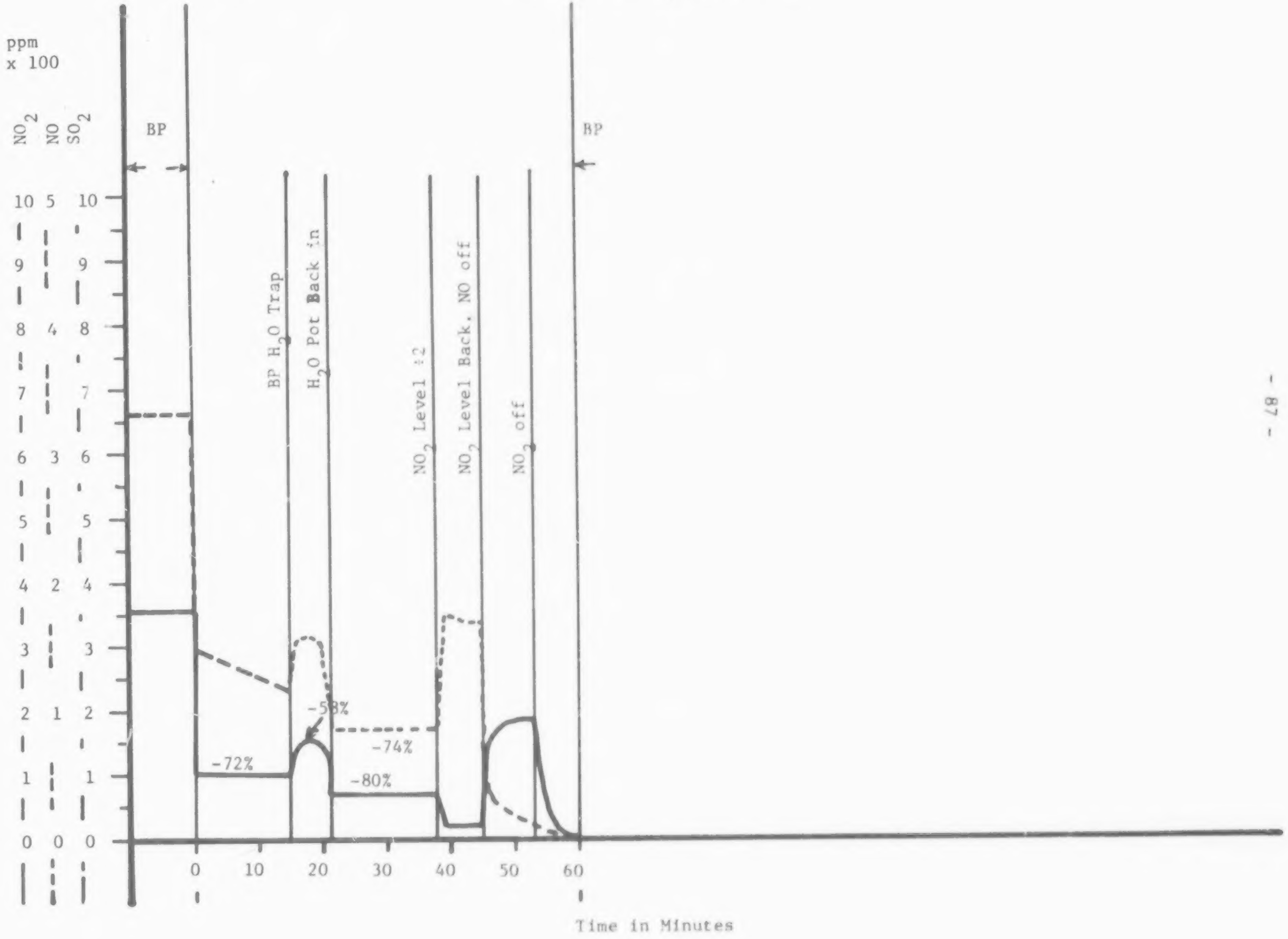
(2) From 120 -> 180 min. Δ NO ≈ 59%, Δ NO_2 ≈ 56%. This is more than the sum of the parts for each individual bath.

(3) Are probably stripping NH_3 from first pot & transferring to second pot to produce a scrub of NH_4OH + NH_4OAc. This is not possible when each pot is run separately. Thus, the scrubbers are much more efficient in series because of NH_4OH scrubber, which is known to be a good scrub by itself.

(4) Could smell NH_3 being stripped from first scrub. No odor after passing thru H_2SO_4.

NO: H_2SO_4 (sat'd with NO · NO_2) ⟶ dry ice ⟶ NDIR

1-26-72 28% NH_4OH and H_2O in Series



NOX SCRUBBING DATA SHEET

DATE: 1-26-72 SCRUB: 28 wt. % NH_4OH & H_2O dual bath sequence

OBJECT: Free pickup of NH_3 in water bath & subsequent scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

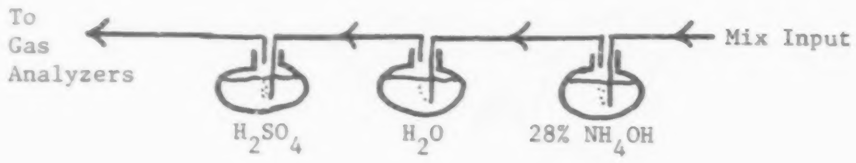
Pot Temp. 70 °F Initial pH - Final pH -

H_2O 10 % CO_2 12 % O_2 3 %

NO 330 ppm NO_2 355 ppm SO_2 ppm

COMMENT:

(1)



Pot "C" (NH_4OH) warmed from ≈ 70°F ->86°F over ≈ 20 min. & then cooled down to 65°F.

The water (pot B) went from ≈ 73°F -> 113°F over the run.

The H_2SO_4 (pot A) went from ≈ 73°F -> 83°F

(2) NO_2 is necessary for NO absorption.

NO: H_2SO_4 -> HOAc · Na_2SO_3 -> dry ice -> NDIR

NOX SCRUBBING DATA SHEET

DATE: 1-26-72 SCRUB: 2.3 Molal Na_2S

OBJECT: Absorb NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 120 °F Initial pH 12 Final pH ______

H_2O 10 % CO_2 12 % O_2 3 %

NO 350 ppm NO_2 350 ppm SO_2 - ppm

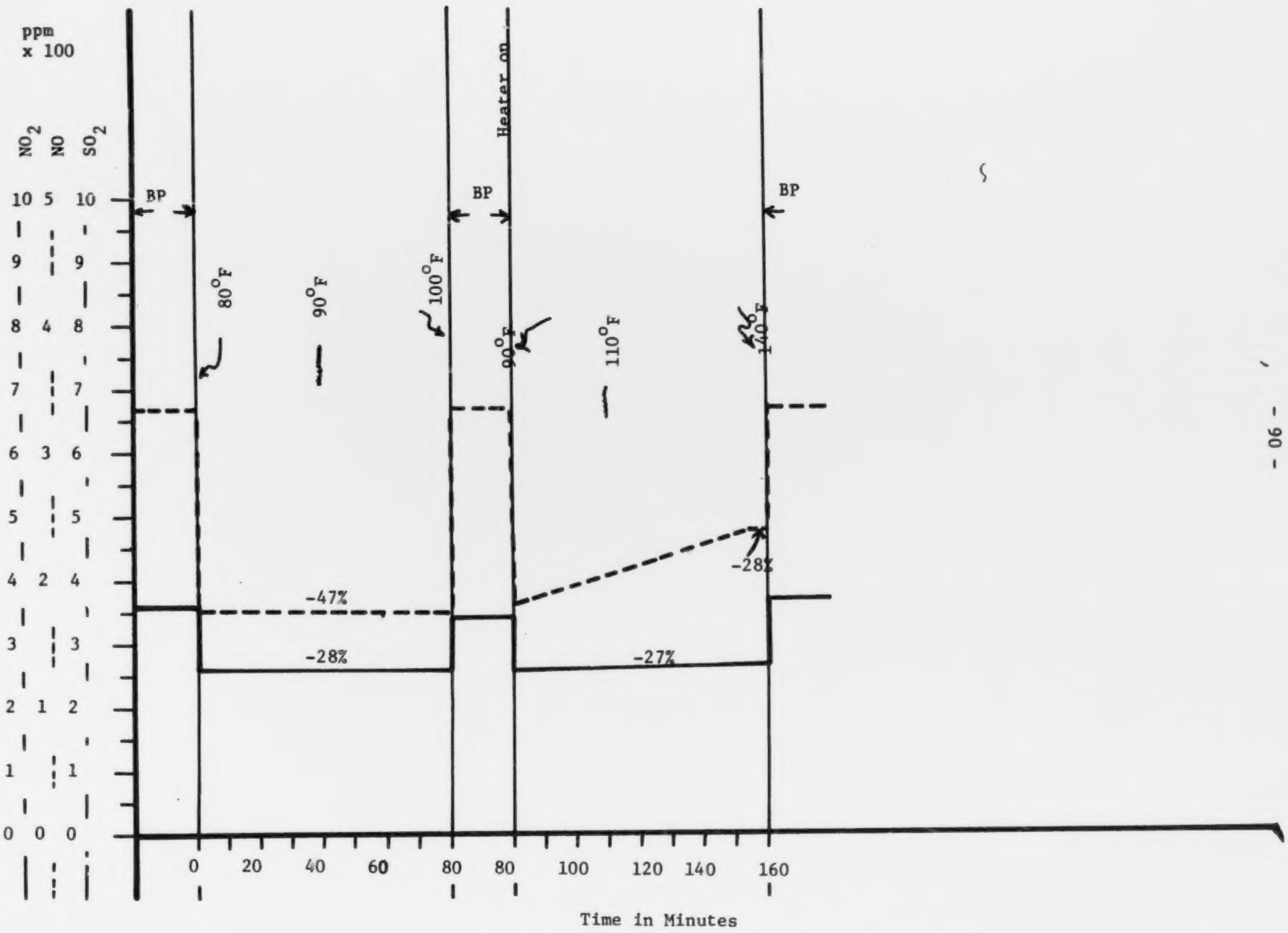
COMMENT:

(1) An attempt to use drierite rather than the Dry Ice trap failed, the drierite generating NO from NO_2 & also not stopping all the H_2O. The system being fouled, the run was unsatisfactory.

(2) The one definite result is that 100% of the NO_2 was absorbed. If any NO was absorbed, it was minor.

1-27-72

14.8 Molal NaOH



NOX SCRUBBING DATA SHEET

DATE: 1-27-72

SCRUB: 14.8 Molal NaOH (same conc. as 28 wt. % NH_4OH)

OBJECT: Comparison of NaOH & NH_4OH

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

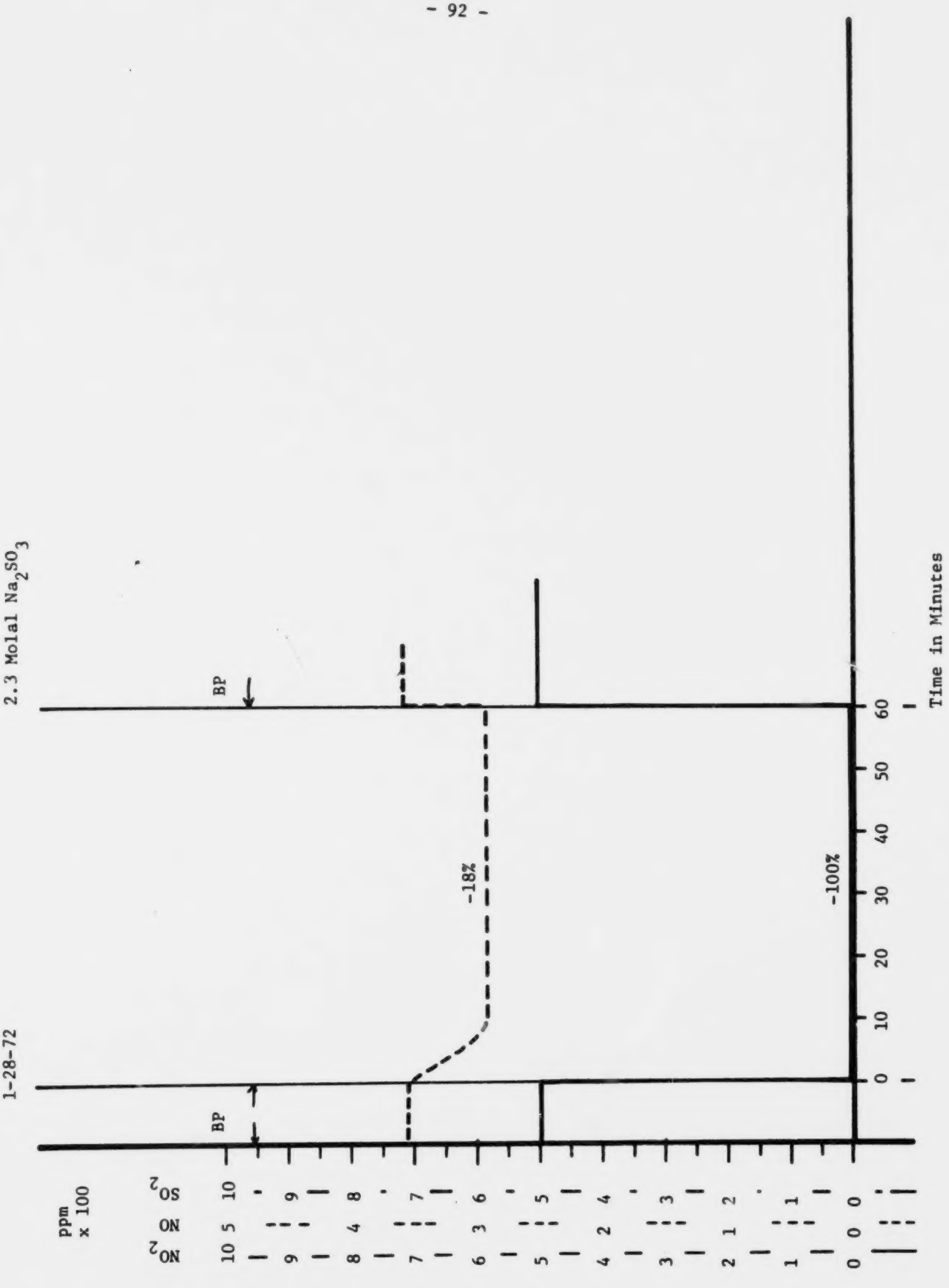
Pot Temp.	varies °F	Initial pH	-	Final pH	-
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	333 ppm	NO_2	360 ppm	SO_2	- ppm

COMMENT:

(1) Had to use an open tube on the scrubber because the frit tended to clog. (Probably with Na_2CO_3)

(2) Temperature rose due to heat liberated upon CO_2 absorption.

NO: Dry Ice trap -> NDIR (≃ 25% NO_2 conv. -> NO in trap)


1-28-72
2.3 Molal Na_2SO_3
BP
BP
-18%
-100%
ppm x 100
NO_2
NO
SO_2
10 10 5
9 9
8 8 4
7 7
6 6 3
5 5
4 4 2
3 3
2 2 1
1 1
0 0 0
0
10
20
30
40
50
60
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 1-28-72 SCRUB: Na_2SO_3, 2.3 Molal

OBJECT: Absorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 120-125 °F Initial pH 10 Final pH -

H_2O 10 % CO_2 12 % O_2 3 %

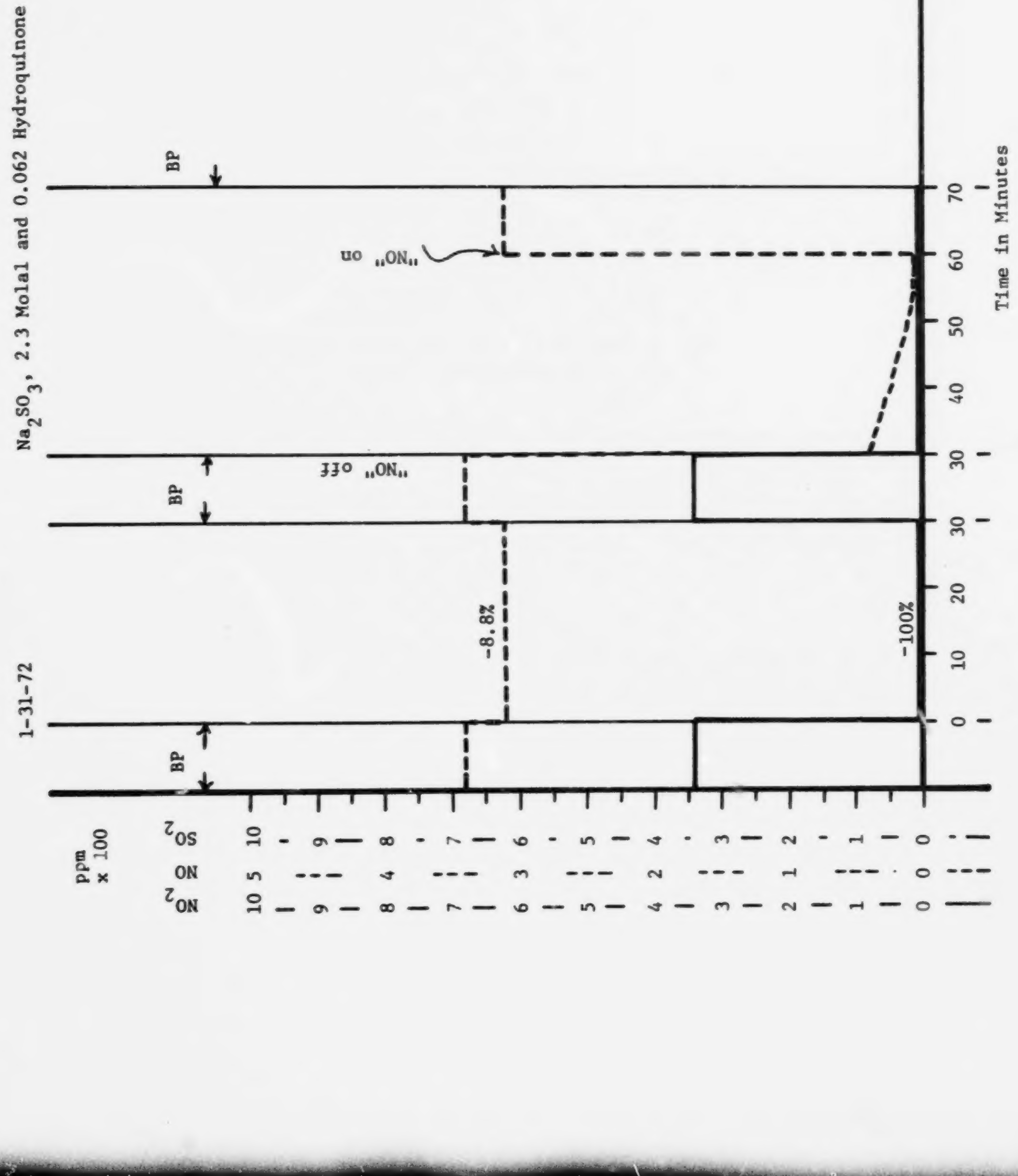
NO 355 ppm NO_2 500 ppm SO_2 ppm

COMMENT:

(1) Δ NO = 18% Δ NO_2 = 100%

(2) After 60 minutes on line, solution analysis gave 2.0 millimoles of NO_3^- and 0.4 millimoles of NO_2^-.

NO: Wet Ice Trap -> NDIR


Na$_2$SO$_3$, 2.3 Molal and 0.062 Hydroquinone

1-31-72

NOX SCRUBBING DATA SHEET

DATE: 1-31-72

SCRUB: 2.3 Molal Na_2SO_3 with Hydroquinone 0.062 Molal

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 123 °F
Initial pH 10
Final pH -

H_2O 10 %
CO_2 12 %
O_2 3 %

NO 340 ppm
NO_2 340 ppm
SO_2 - ppm

COMMENT:

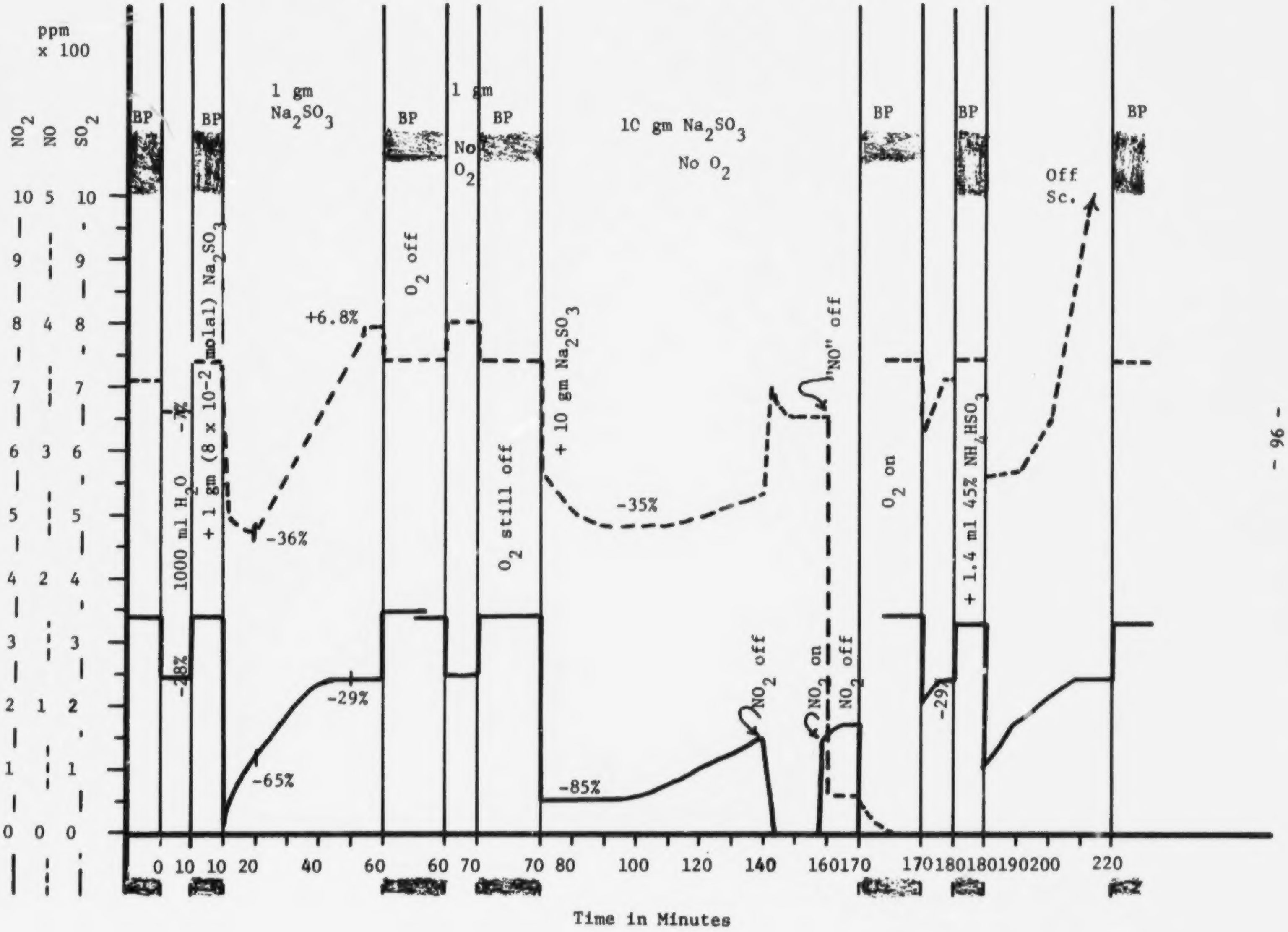
(1) Δ NO = 8.8%
Δ NO_2 = 100%

(2) NO not required for NO_2 absorption.

NO: Dry Ice Trap -> NDIR

2-1-72

Various Levels of $SO_3^=$ as Na_2SO_3 and NH_4HSO_3



NOX SCRUBBING DATA SHEET

DATE: 2-1-72 SCRUB: Varing levels of SO_3 = with Na_2SO_3 & NH_4HSO_3

OBJECT: See effect of concentration and of oxygen

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH - Final pH -

H_2O 10 % CO_2 12 % O_2 3 %

NO 355 ppm NO_2 340 ppm SO_2 - ppm

COMMENT:

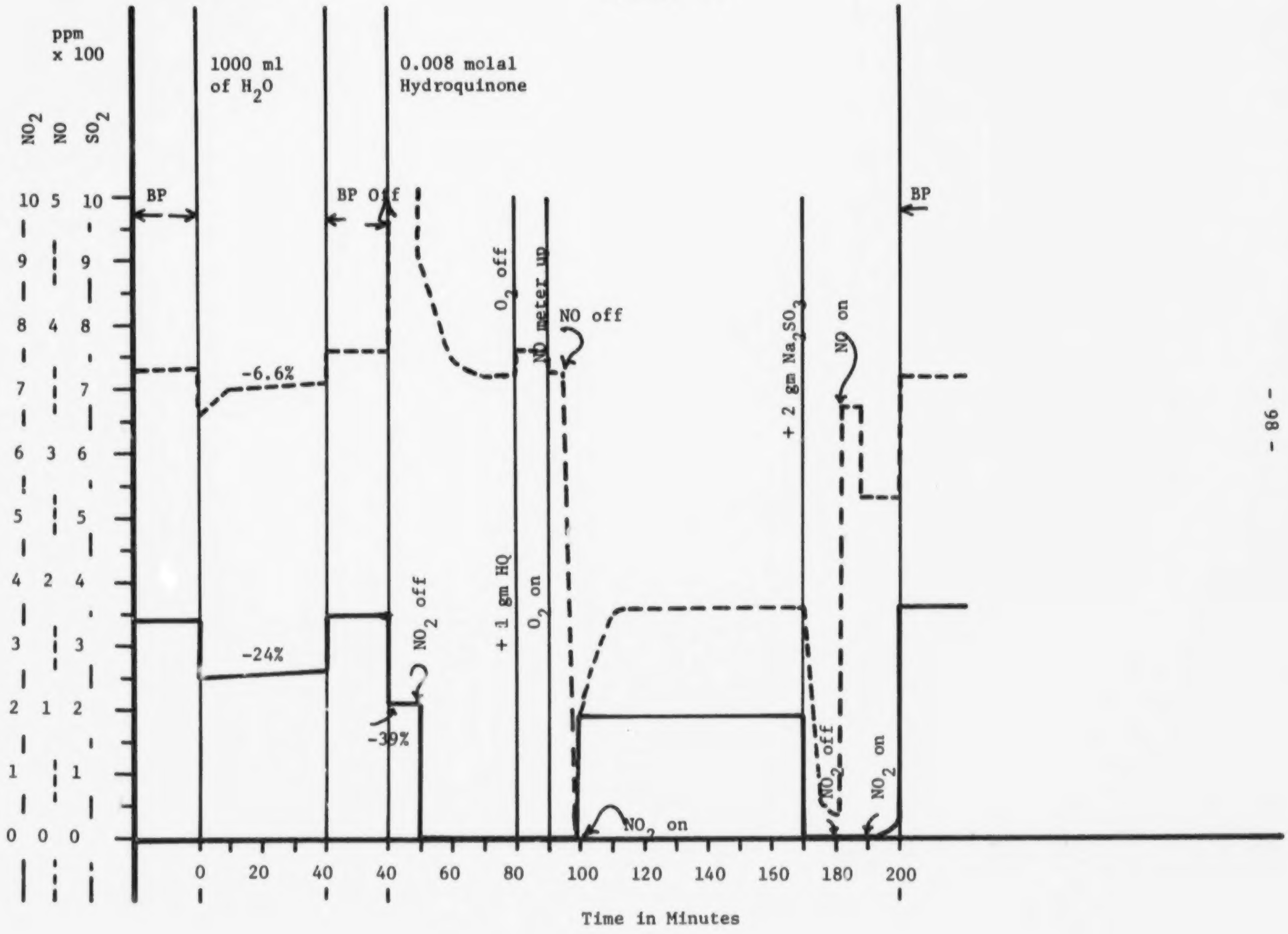
(1) With 1 gm/liter of Na_2SO_3, the initial absorption is ≈ 100% NO_2 & 36% NO. This diminishes to ≈ 29% NO_2 (same as H_2O) with 6.8% generated (also same as H_2O).

(2) The elimination of O_2 from the 1st bath has no effect.

(3) 10 gm per litre of Na_2SO_3 => 85% NO_2 & 35% NO for ≈ 30 min. It them starts behaving like the 1 gm bath.

(4) The small level of NH_4HSO_3 behaves similarly except generating an off scale NO signal.

NO: Dry Ice Trap -> NDIR (≈ 24% conv. of NO_2 to NO)



2-2-72

Hydroquinone

NOX SCRUBBING DATA SHEET

DATE: 2-2-72 SCRUB: Hydroquinone

OBJECT: Effect of anti-oxidant

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F Initial pH - Final pH -

H_2O 10 % CO_2 12 % O_2 3 %

NO 365 ppm NO_2 340 ppm SO_2 - ppm

COMMENT:

(1) H_2O blank @ Δ NO = 6.6%, Δ NO_2 24%

(2) On line with HQ & the Δ NO_2 = = 39%. The NO signal exceeded the scale.

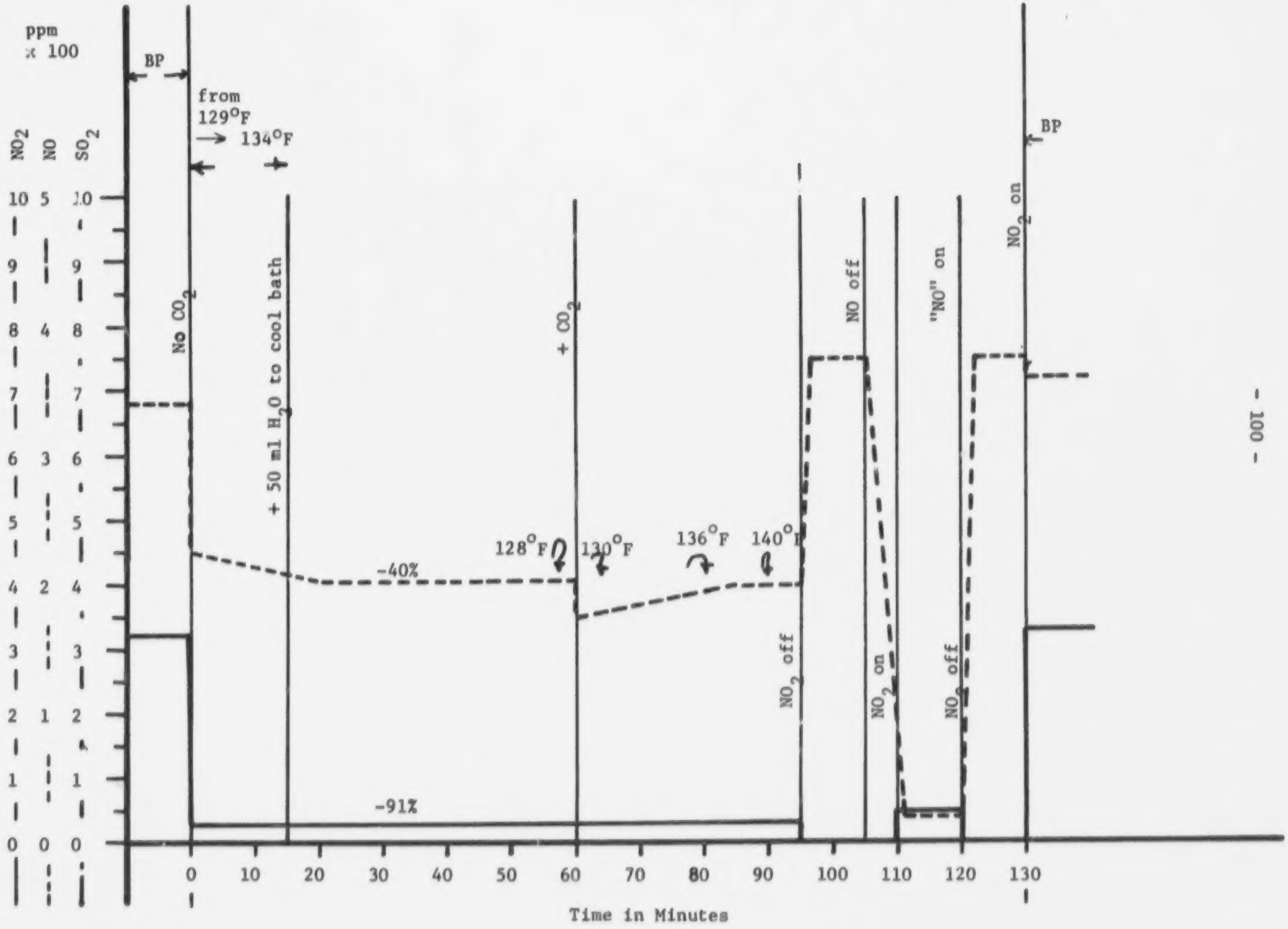
(3) With the NO off & the NO_2 on, 50% of the NO_2 was converted to NO with a Δ NO_2 of = 50%.

(4) Solution turned red with Na_2SO_3 addition.

NO: Dry Ice Trap -> NDIR

2-3-72

2-Amino Ethanol



NOX SCRUBBING DATA SHEET

DATE: 2-3-72 SCRUB: 2-Amino Ethanol

OBJECT: Adsorb NOX

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. Varies °F Initial pH ______ Final pH ______

H_2O 10 % CO_2 12 % O_2 3 %

NO 340 ppm NO_2 320 ppm SO_2 -- ppm

COMMENT:

(1) Bath temperature with NO_x absorption (NO CO_2). With CO_2, it heated even more rapidly.

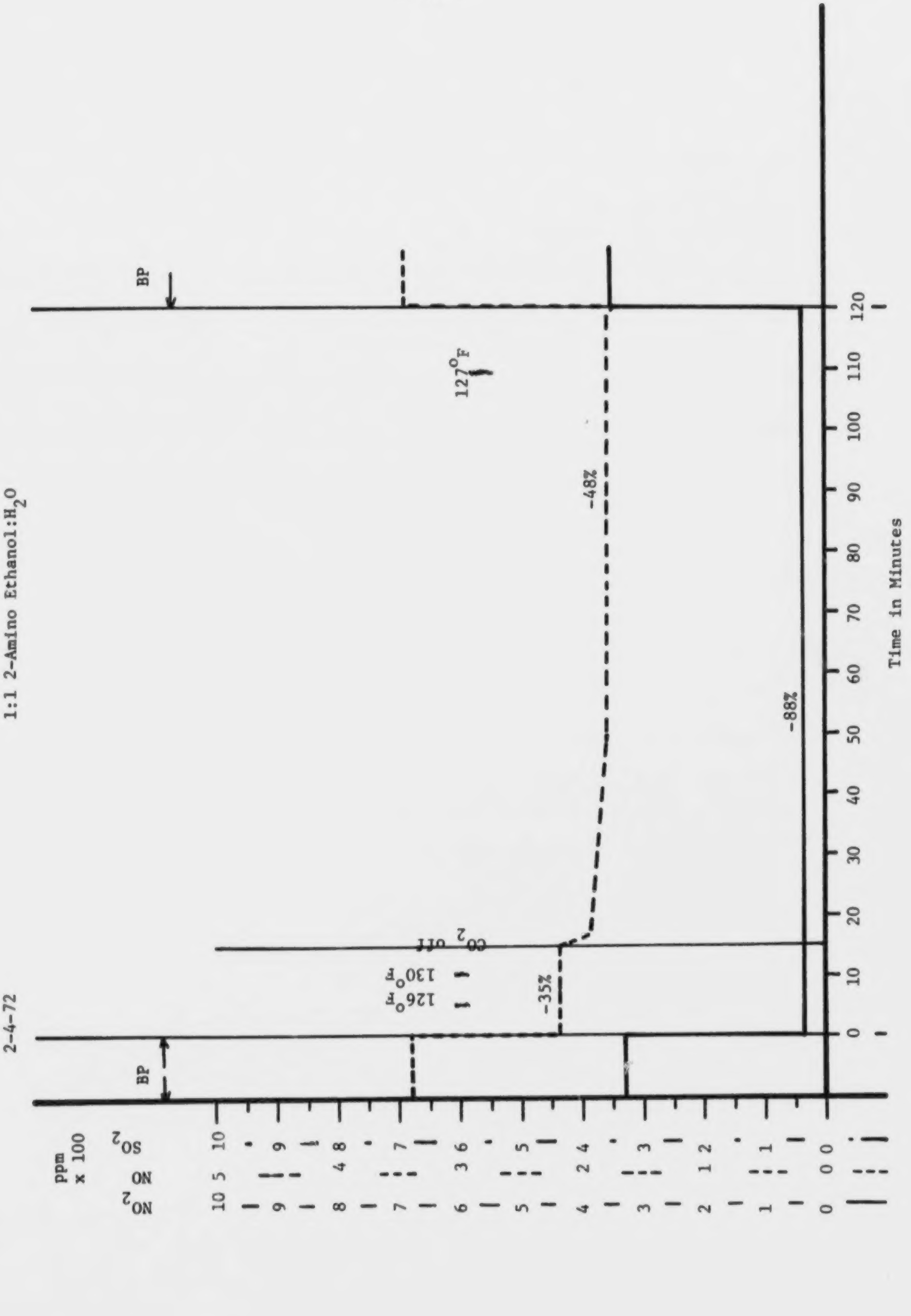
(2) The bath developed a mist over it when NO_2 was run in.

(3) Δ NO ≈ 40% Δ NO_2 ≈91%

(4) H_2SO_4 (dilute) trap used to absorb amine vapors before effluent enters gas analyzers.

(5) Color of bath changed from colorless to orange as run progressed.

NO: $H_2SO_4 \rightarrow$ Dry Ice $\longrightarrow$ NDIR


1:1 2-Amino Ethanol:H$_2$O
2-4-72
BP
BP
126°F
130°F
CO$_2$ off
-35%
-48%
-88%
127°F
Time in Minutes
0
10
20
30
40
50
60
70
80
90
100
110
120
ppm x 100
NO$_2$
NO
SO$_2$
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 2-4-72 SCRUB: 1:1, 2-Amino ethanol: H_2O

(volume ratio)

OBJECT: Absorb NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

NO 340 ppm NO_2 330 ppm SO_2 ppm

COMMENT:

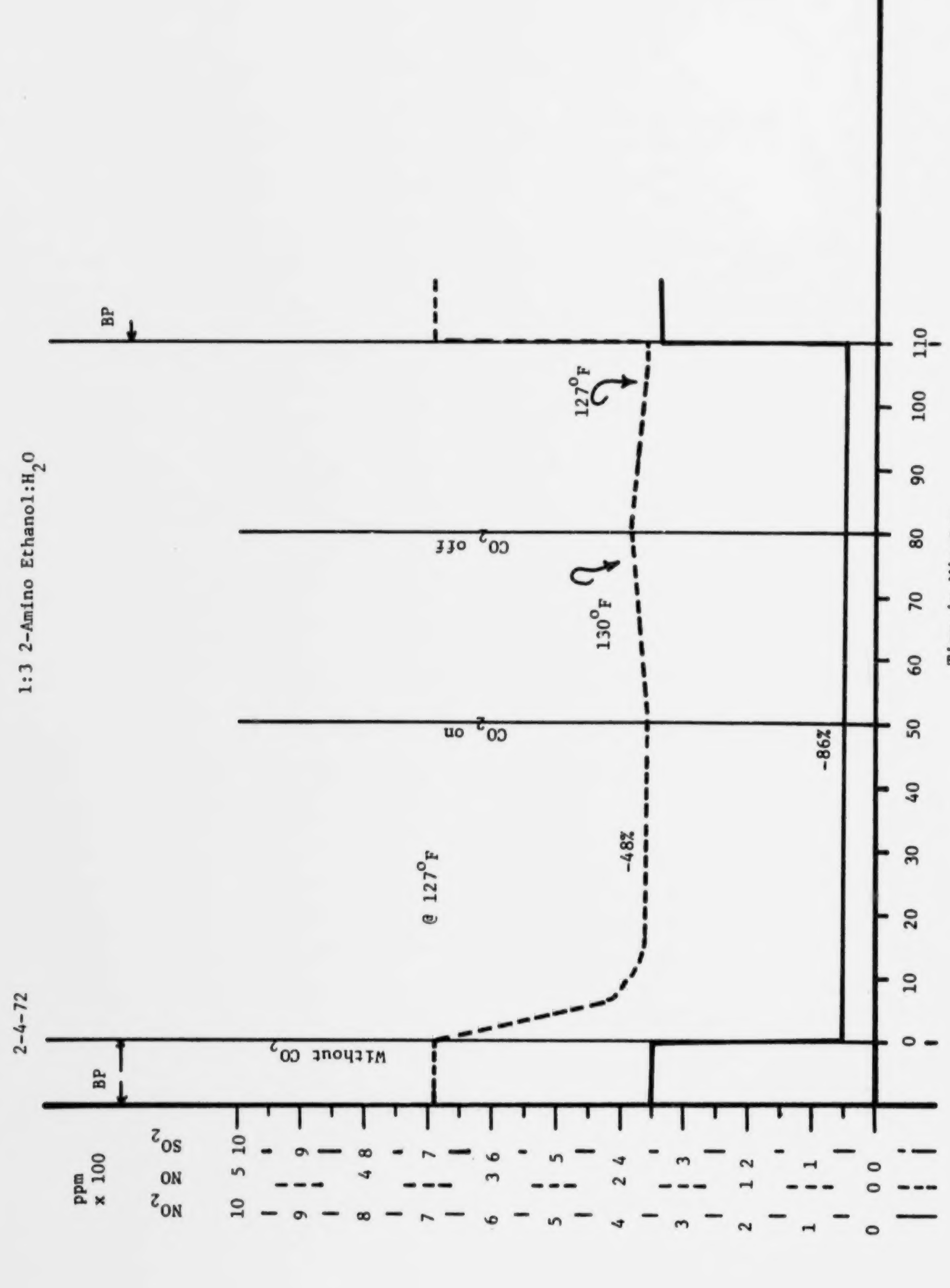
(1) With CO_2 present 35% of NO and 88% of NO_2 absorbed.

(2) Without CO_2, 48% NO and 88% NO_2 absorbed.

(3) Bath heats up from reaction with CO_2

(4) H_2SO_4 trap removed amine vapors from gas stream

NO: H_2SO_4 → Dry ice trap → NDIR


1:3 2-Amino Ethanol:H_2O
2-4-72
ppm x 100
NO_2 NO SO_2
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5
0 2 4 6 8 10
BP
Without CO_2
@ 127°F
-48%
-86%
CO_2 on
CO_2 off
130°F
127°F
BP
0 10 20 30 40 50 60 70 80 90 100 110
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 2-4-72

SCRUB: 1:3, 2-Amino ethanol: water (volume ratio)

OBJECT: Absorb NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	127 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	347 ppm	NO_2	350 ppm	SO_2	-- ppm

COMMENT:

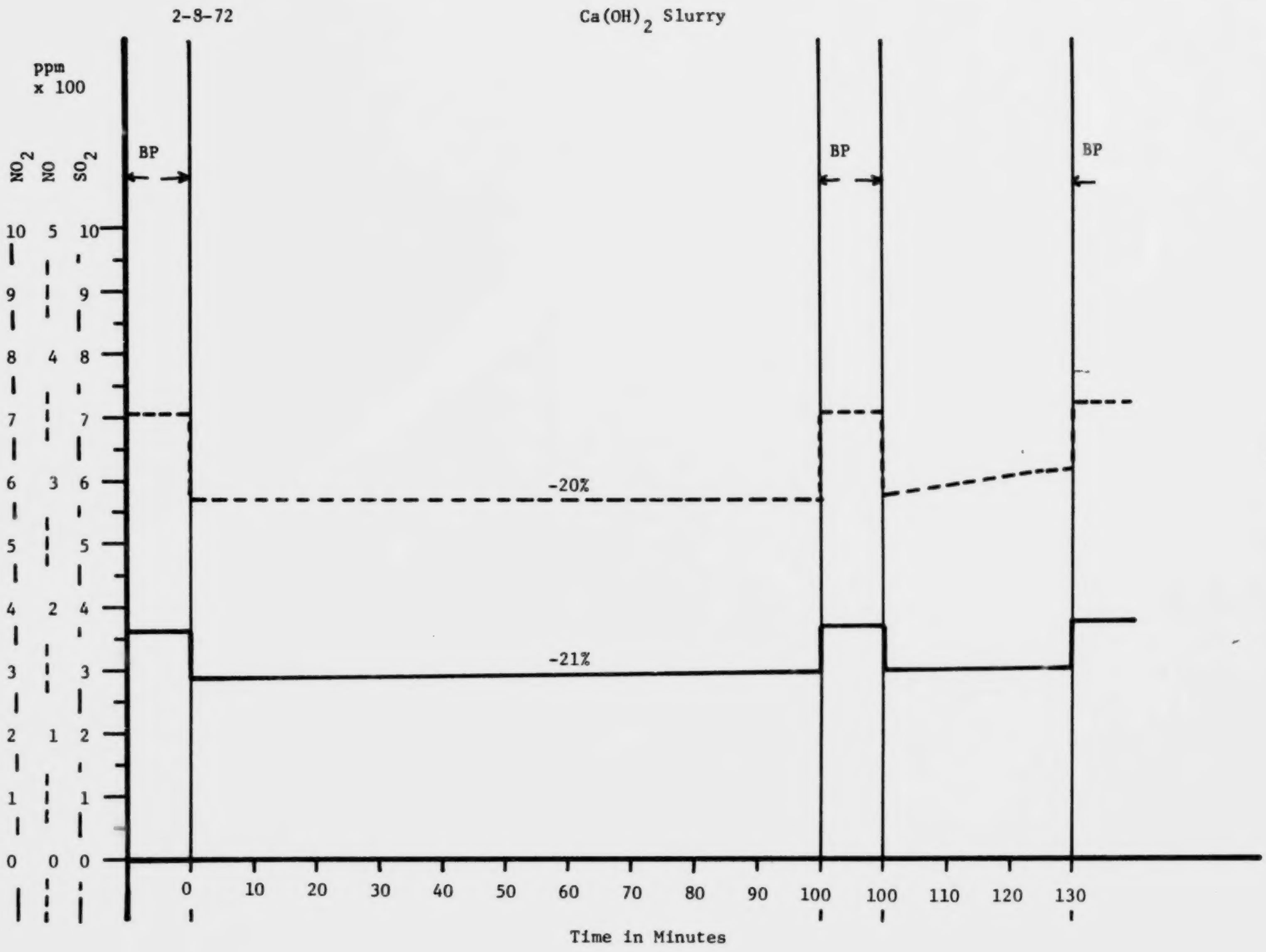
(1) Δ NO (without CO_2) $\approx$ 48%
Δ NO_2 $\approx$ 86%

(2) The addition of CO_2 caused bath heating

(3) Takes about 35 minutes to saturate dilute H_2SO_4 trap with NO and NO_2, before starting run.

(4) H_2SO_4 used to remove amine vapor before analysis

NO: $H_2SO_4 \longrightarrow$ Dry ice $\longrightarrow$ NDIR


2-8-72
Ca(OH)$_2$ Slurry
ppm
x 100
NO_2
NO
SO_2
BP
BP
BP
-20%
-21%
0
10
20
30
40
50
60
70
80
90
100
100
110
120
130
Time in Minutes
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0

NOX SCRUBBING DATA SHEET

DATE: 2-8-72

SCRUB: $Ca(OH)_2$, 100 gm suspended in 1000 ml H_2O

OBJECT: Slurry scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

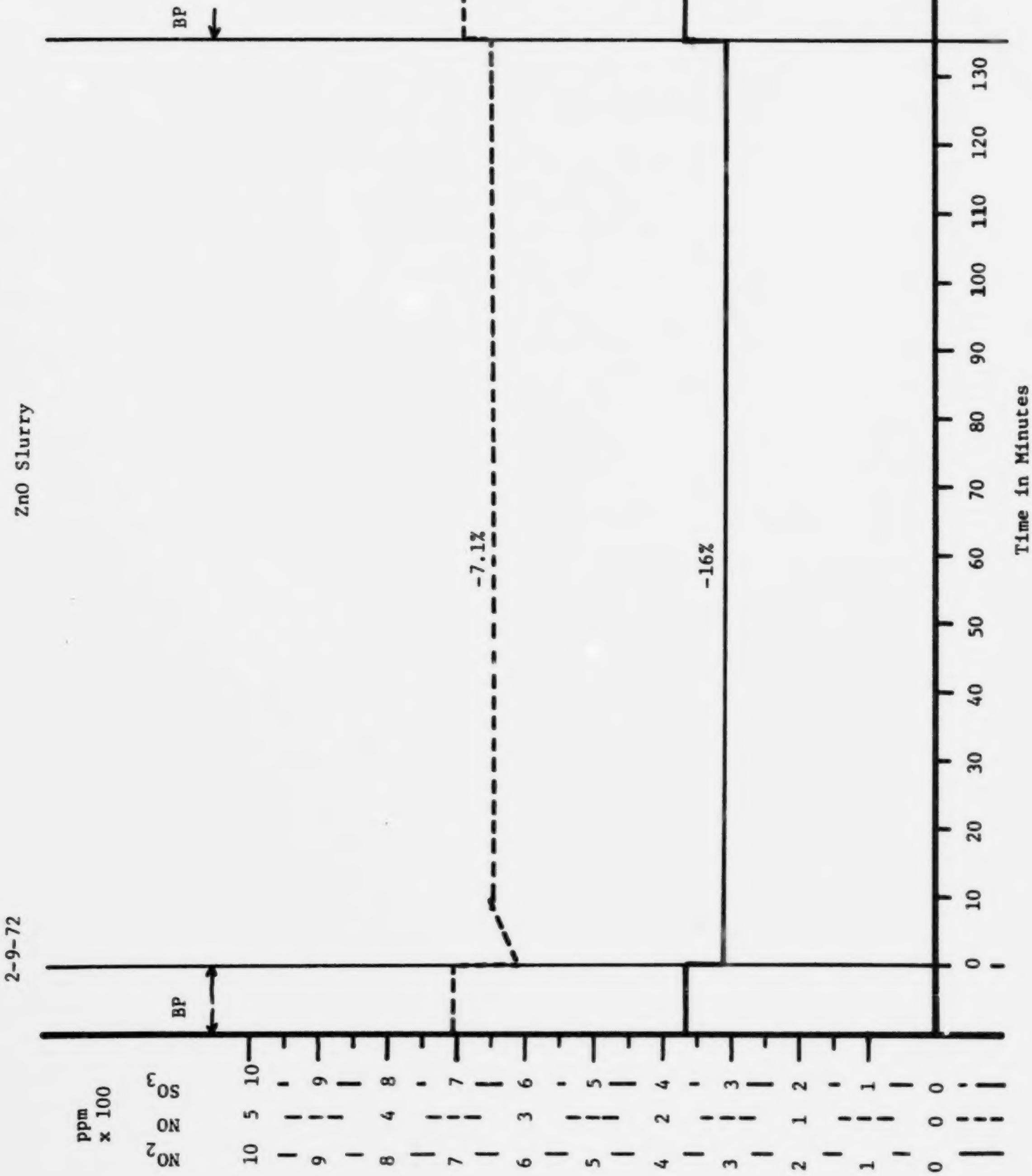
NO 353 ppm NO_2 365 ppm SO_2 ______ ppm

COMMENT:

(1) The frit plugged and an open tube had to be used.

(2) Δ NO $\simeq$ 20% Δ NO_2 $\simeq$ 21%

NO: $NaOH\text{-}Na_2S \longrightarrow$ Dry ice $\longrightarrow$ NDIR


ZnO Slurry
2-9-72
BP
BP
-7.1%
-16%
Time in Minutes
0
10
20
30
40
50
60
70
80
90
100
110
120
130
ppm
x 100
NO_2
NO
SO_3
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 2-9-72 SCRUB: ZnO slurry (100 gm/10000 ml H_2O)

OBJECT: Absorb NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 121 °F Initial pH -- Final pH --

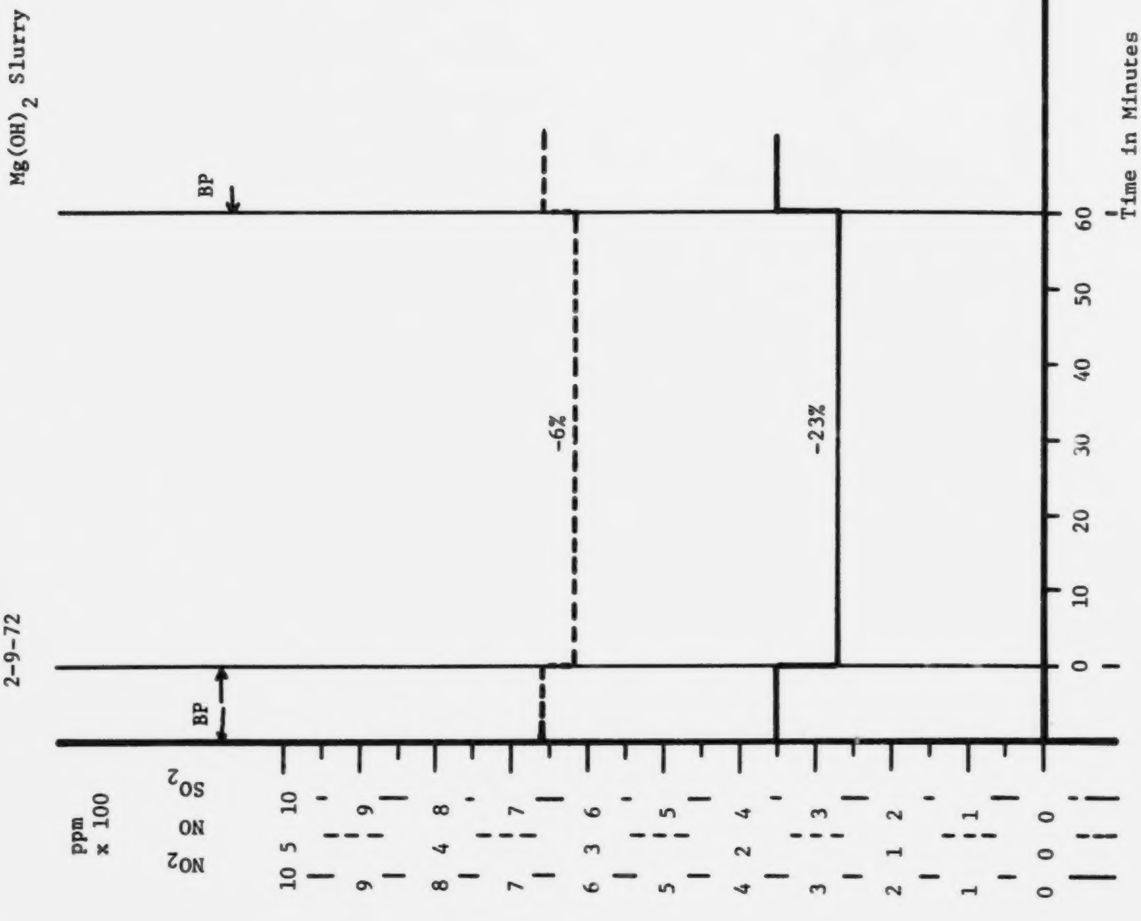
H_2O 10 % CO_2 12 % O_2 3 %

NO 353 ppm NO_2 370 ppm SO_2 ppm

COMMENT:

(1) Δ NO = 7.1%, Δ NO_2 = 16%

NO: Na_2S-NaOH ⟶ Dry ice ⟶ NDIR


2-9-72
Mg(OH)$_2$ Slurry
BP
BP
-6%
-23%
Time in Minutes
0
10
20
30
40
50
60
ppm x 100
NO$_2$
NO
SO$_2$
10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1 0
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 2-9-72

SCRUB: $Mg(OH)_2$ 100 gm/liter slurry in H_2O

OBJECT: Absorb NO_x

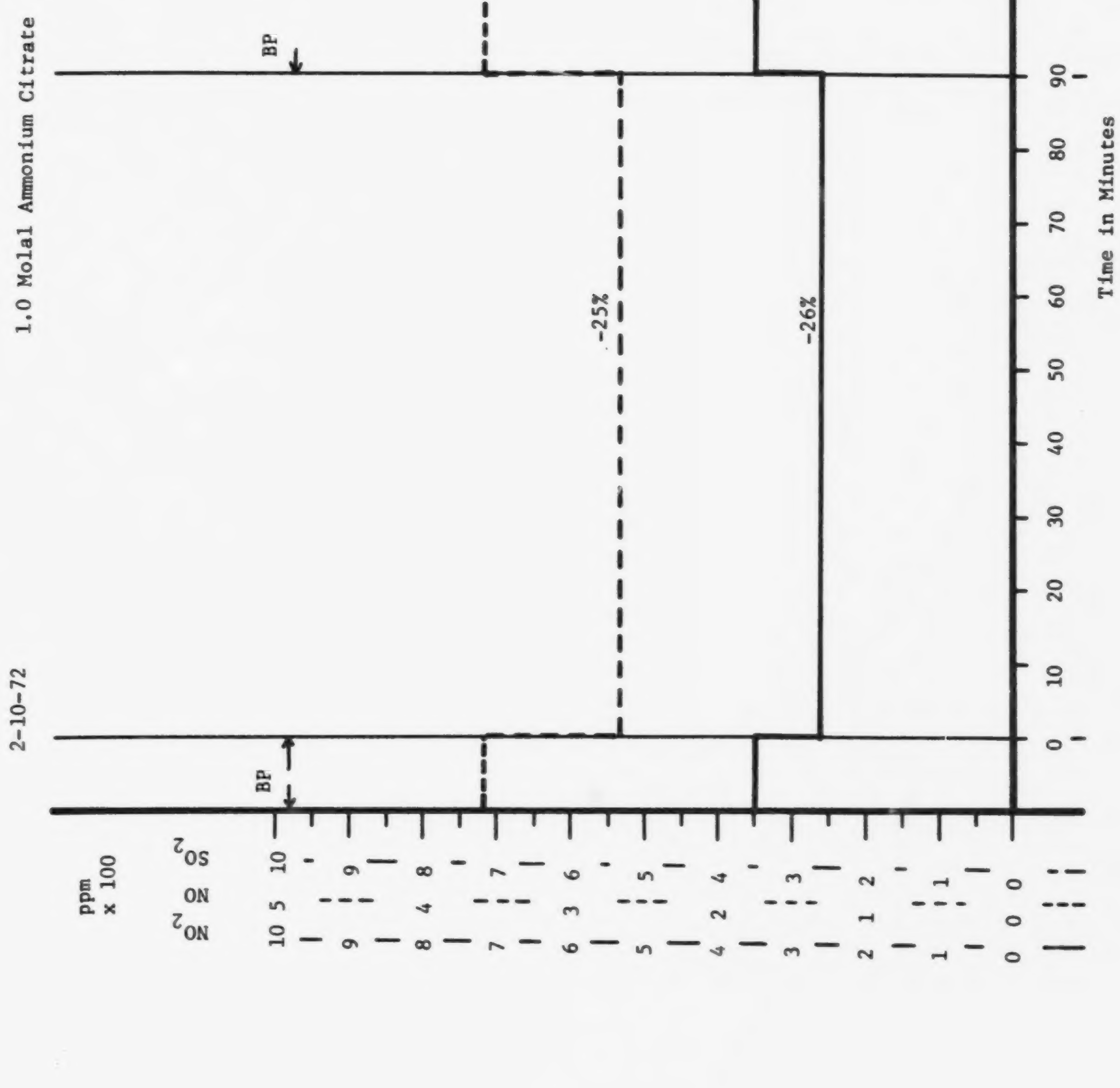
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	330 ppm	NO_2	350 ppm	SO_2	-- ppm

COMMENT:

(1) Δ NO $\approx$ 60%, Δ NO_2 $\approx$ 23%

NO: Na_2S-NaOH ⟶ Dry ice ⟶ NDIR


1.0 Molal Ammonium Citrate
2-10-72
BP
BP
-25%
-26%
Time in Minutes
0
10
20
30
40
50
60
70
80
90
ppm
x 100
NO2
NO
SO2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0

NOX SCRUBBING DATA SHEET

DATE: 2-10-72 SCRUB: 1.0 Molal $(NH_4)_2HC_6H_5O_7$

(ammonium citrate)

OBJECT: Absorb NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH -- Final pH --

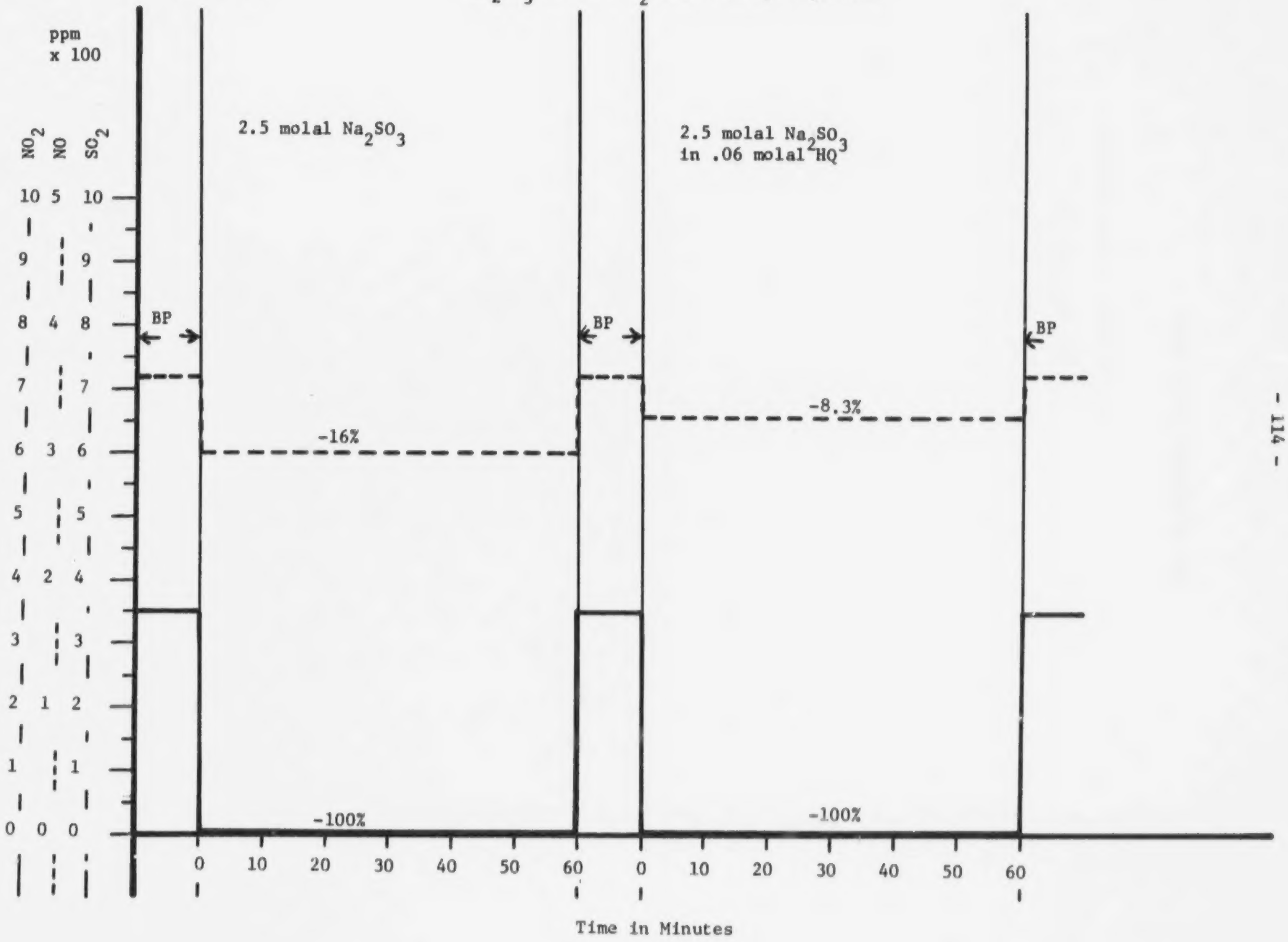
H_2O 10 % CO_2 12 % O_2 3 %

NO 358 ppm NO_2 350 ppm SO_2 ppm

COMMENT: (1) Pulled out 100% of 470 ppm SO_2 in run with NO and NO_2 but seemed to generate NO. SO_2 into sulfide trap produces some H_2S. Thus Na_2S trap was followed by NaOH trap.

NO: $Na_2S \longrightarrow$ Dry ice $\longrightarrow$ NDIR

Na_2SO_3 with no O_2 and with Hydroquinone



NOX SCRUBBING DATA SHEET

DATE: 2-15-72 SCRUB: 2.5 molal Na_2SO_3 (without and with hydroquinone)

OBJECT: NO_x scrubbing with no O_2 present and observe the effect of hydroquinone addition

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 127 °F Initial pH 10 Final pH

H_2O 10 % CO_2 12 % O_2 0 %

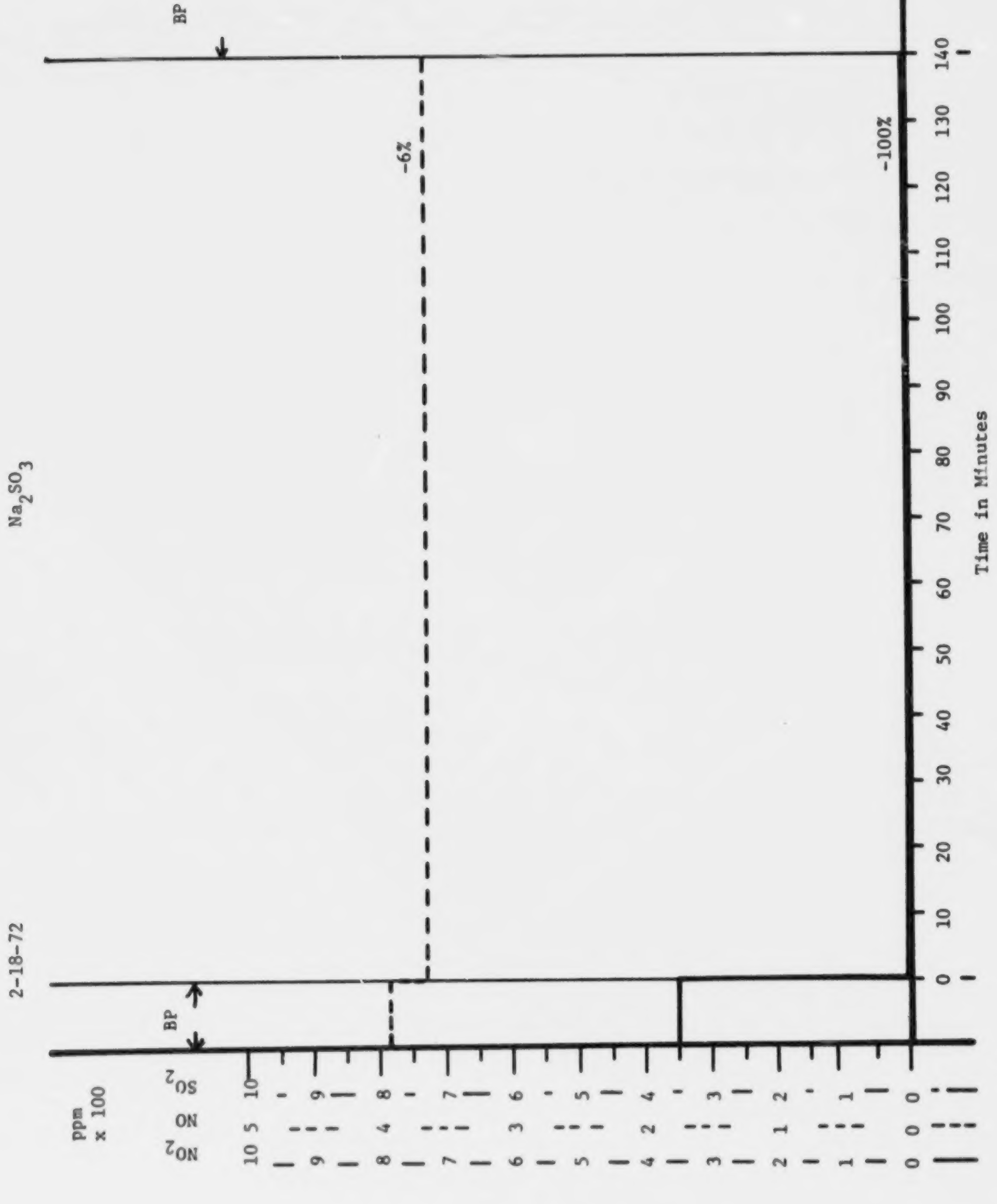
NO 358 ppm NO_2 350 ppm SO_2 -- ppm

COMMENT:

(1) The HQ lowered the efficiency of NO adsorption from 16% to 8.3%.

(2) After 60 minutes on line (before HQ added) solution analysis gave 4.2 millimoles of NO_3 and 1.1 millimoles of NO_2.

NO: $Na_2S \longrightarrow$ Dry ice $\longrightarrow$ NDIR


Na$_2$SO$_3$
2-18-72
BP
BP
-6%
-100%
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time in Minutes
ppm x 100
NO$_2$
10 9 8 7 6 5 4 3 2 1 0
NO
5 4 3 2 1 0
SO$_2$
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 2-18-72 SCRUB: 2.5m Na_2SO_3

OBJECT: Study sulfite scrubbing with O_2 in flue gas

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 127 °F Initial pH ____ Final pH ____

H_2O 10 % CO_2 12 % O_2 3 %

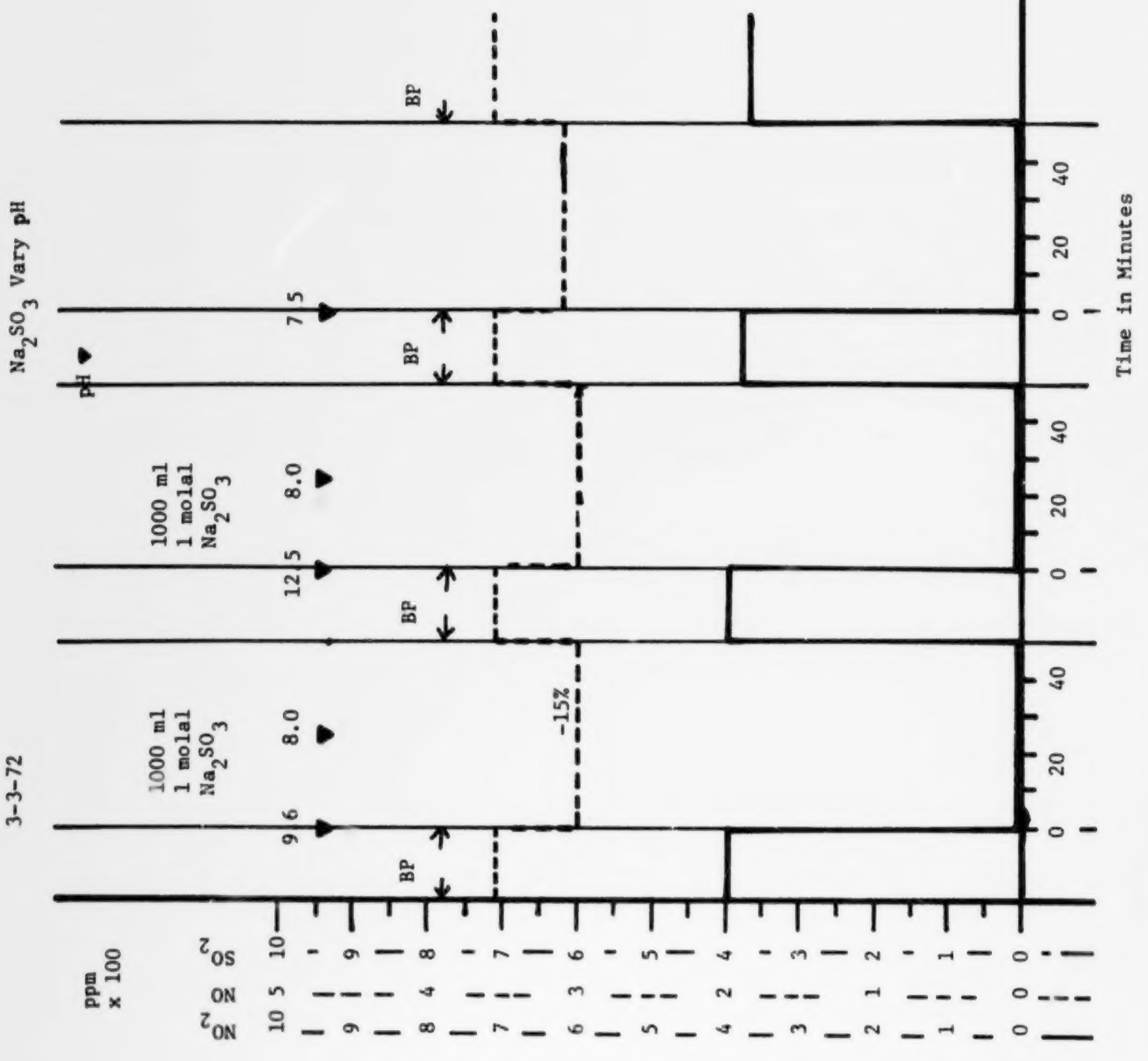
NO 350 ppm NO_2 350 ppm SO_2 -- ppm

COMMENT:

(1) Δ NO_2 = 100%, NO = 6%.

(2) NO & NO_2 meters not operating properly, sticking and pulsing; results questionable.

NO: $Na_2S \longrightarrow$ Dry ice $\longrightarrow$ NDIR


3-3-72
1000 ml
1 molal
Na_2SO_3
9.6
8.0
BP
-15%
1000 ml
1 molal
Na_2SO_3
12.5
8.0
BP
pH ▼
Na_2SO_3 Vary pH
7.5
BP
BP
ppm
x 100
NO_2
NO
SO_2
10 5 10
9 9
8 4 8
7 7
6 3 6
5 5
4 2 4
3 3
2 1 2
1 1
0 0 0
0 20 40
0 20 40
0 20 40
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-3-72 SCRUB: 1.0m Na_2SO_3

OBJECT: Study effect of changing pH

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F Initial pH see chart Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 355 ppm NO_2 400 ppm SO_2 -- ppm

COMMENT:

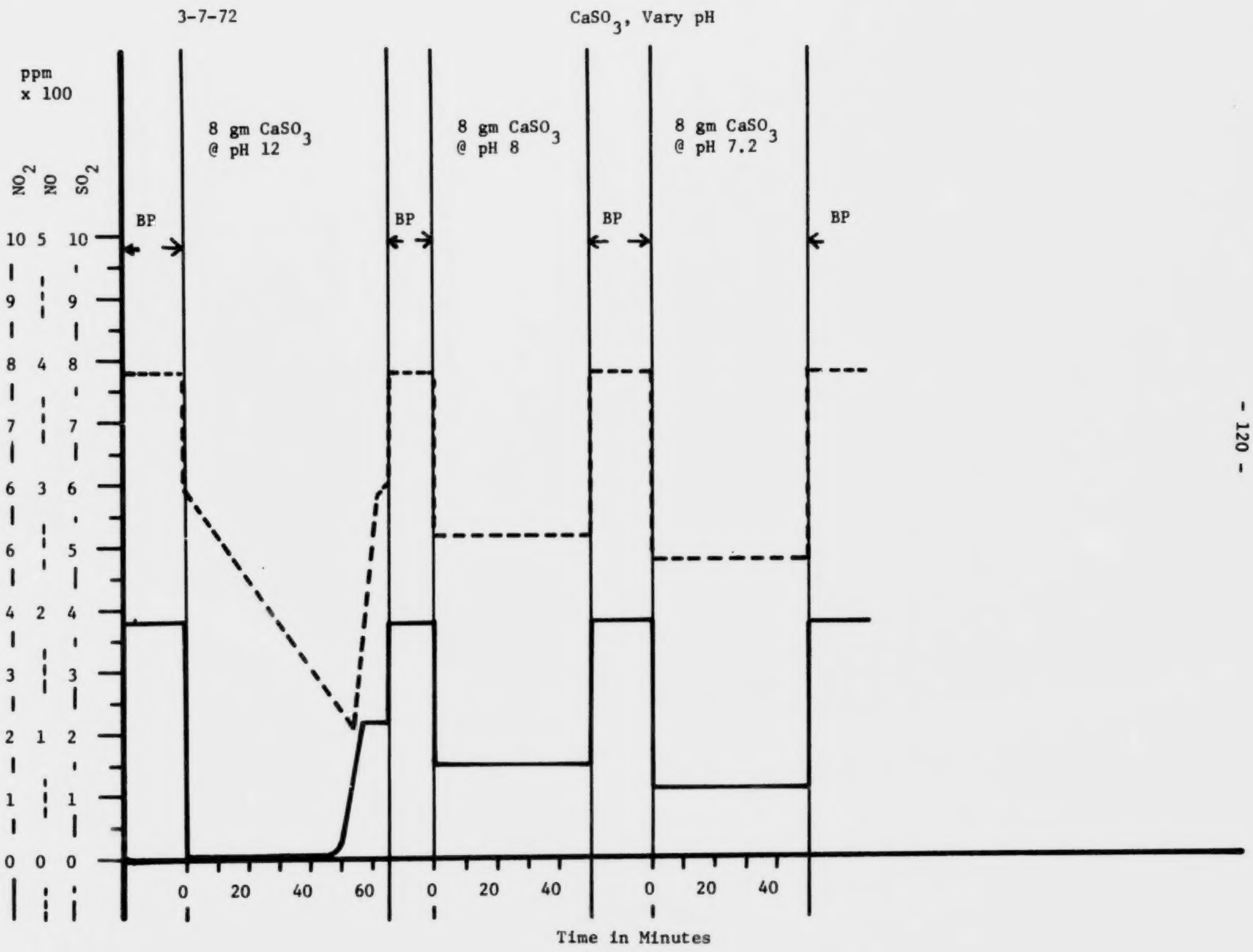
(1) The NO readings were very noisy

(2) The pH made no difference in NO_2 adsorption

(3) The NO absorption changed very slightly, decreasing with decreasing pH.

(4) The pH was increased with NaOH and decreased with HCl.

NO: Na_2S trap ⟶ Dry ice trap ⟶ NDIR


3-7-72
CaSO$_3$, Vary pH
ppm
x 100
NO$_2$
NO
SO$_2$
10 5 10
9 9
8 4 8
7 7
6 3 6
6 5
4 2 4
3 3
2 1 2
1 1
0 0 0
BP
8 gm CaSO$_3$
@ pH 12
BP
8 gm CaSO$_3$
@ pH 8
BP
8 gm CaSO$_3$
@ pH 7.2
BP
0
20
40
60
0
20
40
0
20
40
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-7-72 SCRUB: $CaSO_3$ slurry; 8g/l

OBJECT: Observe effect of pH upon scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH		Final pH	
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	490 ppm	NO_2	380 ppm	SO_2	-- ppm

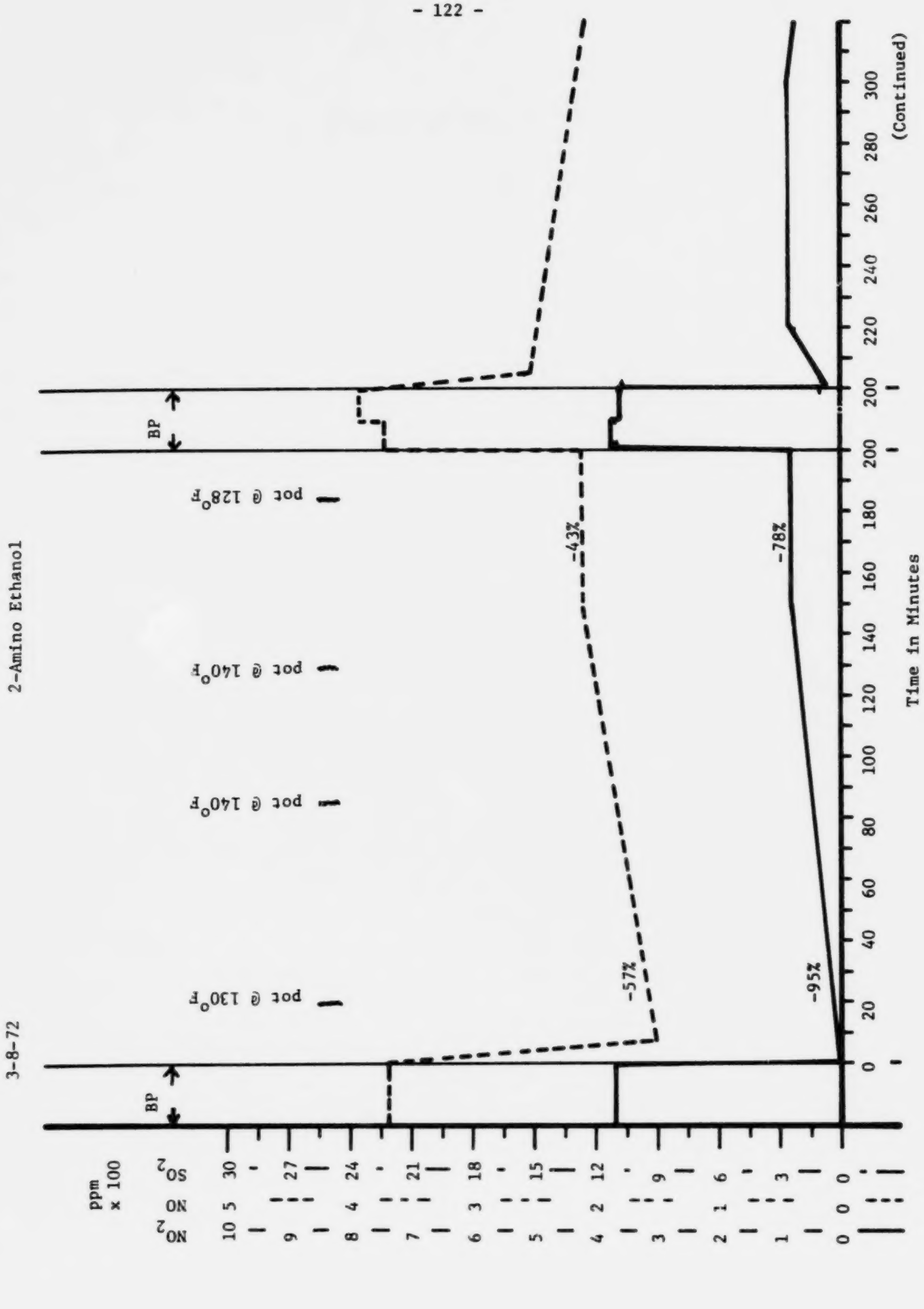
COMMENT:

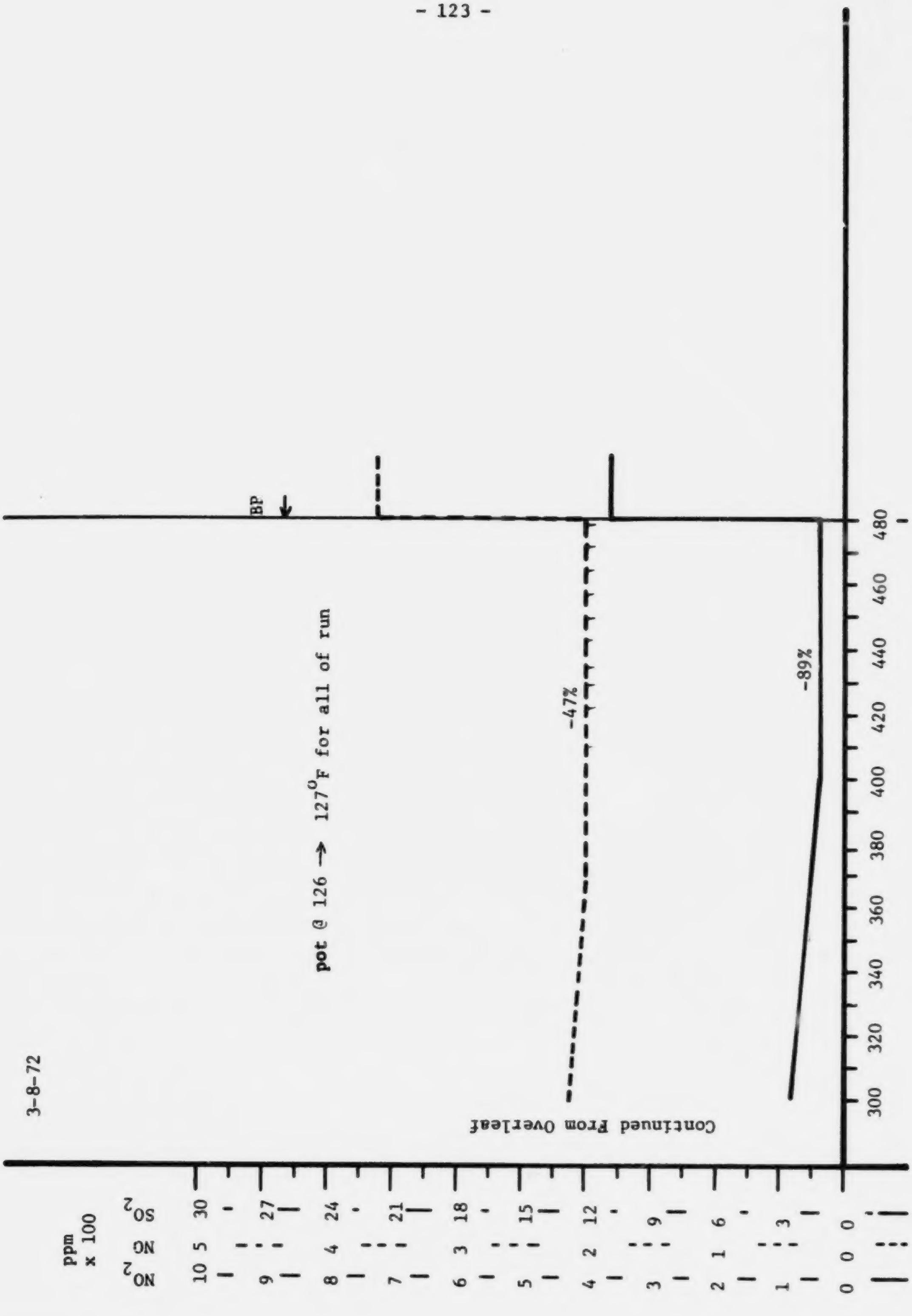
(1) The NO readings were slightly unsteady.

(2) The most efficient scrubbing occured at pH 12.

(3) pH made basic with NaOH and more acidic with HCl. "Normal" pH slurry is 8.

NO: Na_2S → Dry ice → NDIR


3-8-72
2-Amino Ethanol
BP
BP
pot @ 130°F
pot @ 140°F
pot @ 140°F
pot @ 128°F
-57%
-43%
-95%
-78%
ppm x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
0
20
40
60
80
100
120
140
160
180
200
200
220
240
260
280
300
Time in Minutes
(Continued)


3-8-72
pot @ 126 → 127°F for all of run
BP
-47%
-89%
Continued From Overleaf
300
320
340
360
380
400
420
440
460
480
ppm x 100
NO2 NO SO2
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0

NOX SCRUBBING DATA SHEET

DATE: 3-8-72 SCRUB: 2-Amino ethanol, 25% by volume in H_2O

OBJECT: Determine nitrogen content of solution before and after run.

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	130 °F	Initial pH	NA	Final pH	NA
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	368 ppm	NO_2	370 ppm	SO_2	NA ppm

COMMENT:

(1) The scrubbing of NO_x was fairly good in the beginning but became worse with time. This was probably due to the heating of the pot by an exothermic reaction of the amine with the flue gas (prob. CO_2 plus amine). When the bath cooled down, the scrubbing improved somewhat.

(2) The scrub turned progressively yellow with time and was orange after 8 hours of running.

(3) Measurement of total nitrogen content before and after run (in order to determine gain or loss of nitrogen) was inconclusive.

NO: $H_2SO_4 \rightarrow Na_2S \rightarrow$ Dry ice $\longrightarrow$ NDIR

NOX SCRUBBING DATA SHEET

DATE: 3-10-72

SCRUB: SO_2 - NO_2 interaction in the lines

OBJECT: Observe reaction of pure SO_2 with NO_2 (5%) in the lines

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. NA °F

Initial pH NA

Final pH NA

H_2O 0 %

CO_2 0 %

O_2 0 %

NO 0 ppm

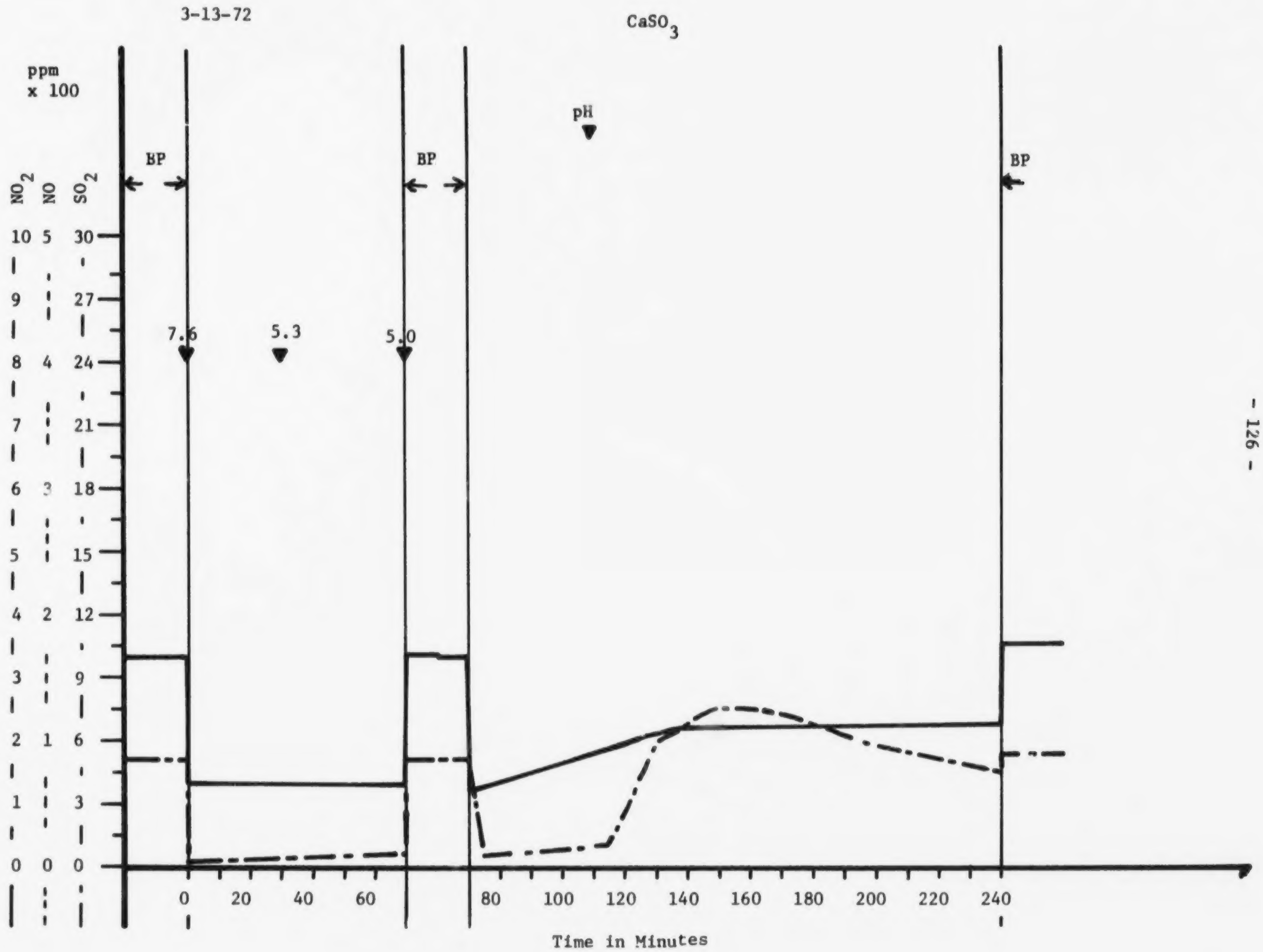
NO_2 varies ppm

SO_2 varies ppm

COMMENT:

(1) With pure SO_2 junctioning with 5% NO_2 in the mix lines, 60 ppm of NO_2 is converted to NO, with a loss of 15 to 30 ppm of SO_2. Neither the temperature of the blending meter (varied from 90 to 350°F) nor the temperature of the analysis lines (75 to 150°F) made a difference.

(2) The problem does not occur if the NO_2 of SO_2 are sufficiently dilute before mixing.


3-13-72
CaSO$_3$
ppm
x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
BP
BP
BP
pH
7.6
5.3
5.0
0
20
40
60
80
100
120
140
160
180
200
220
240
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-13-72 SCRUB: $CaSO_3$ (8 gm per litre of H_2O)

OBJECT: $CaCO_3$ scrubbing with NO_2 solids SO_2 only

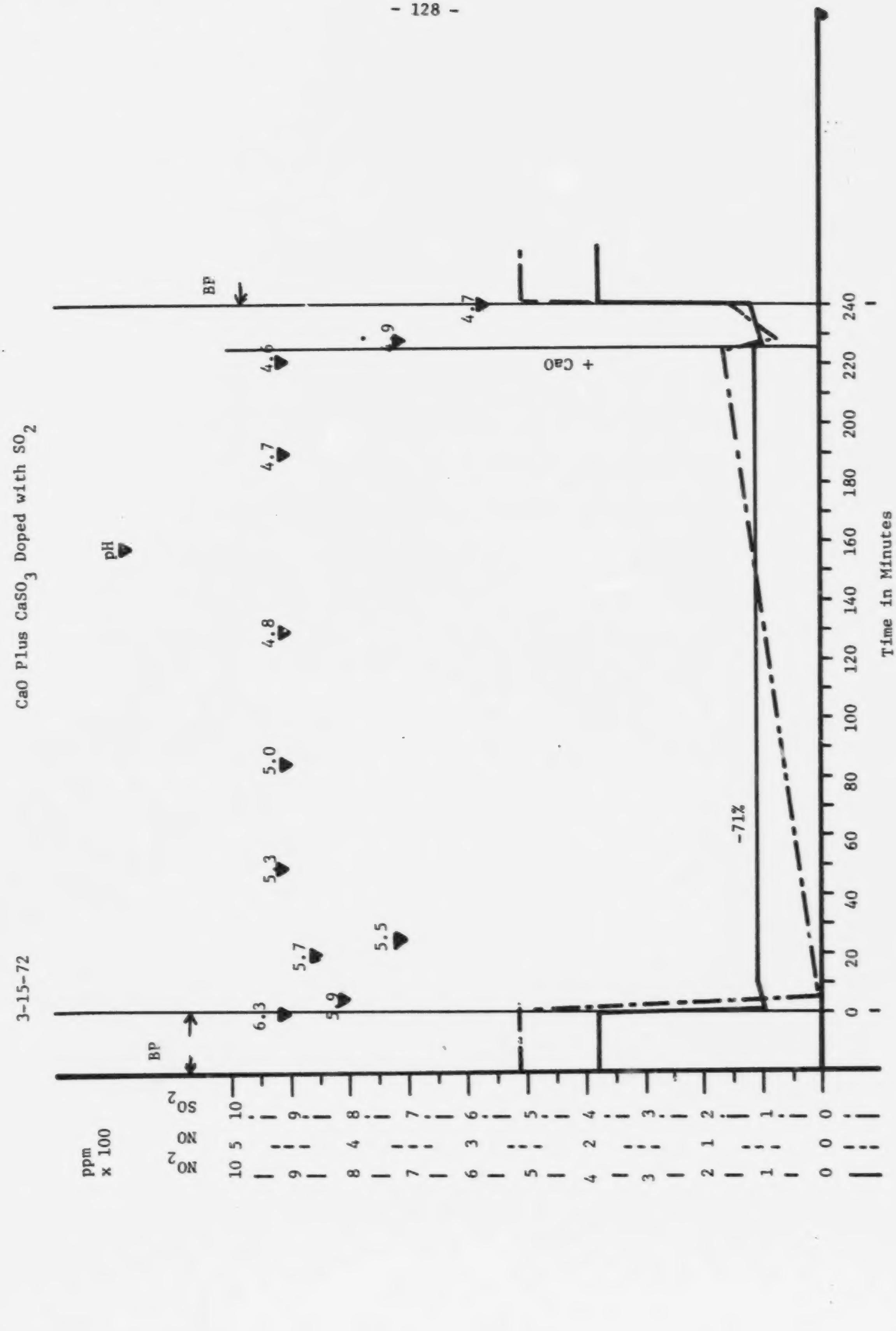
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	7.6	Final pH	
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	330 ppm	SO_2	500 ppm

COMMENT:

(1) The NO_2, in the beginning, was removed quite efficiently. As the pH dropped, and the SO_2 broke through, the NO_2 scrubbing became worse.

NO: Na_2SO_3 ⟶ Dry ice ⟶ NDIR



CaO Plus $CaSO_3$ Doped with SO_2

3-15-72

NOX SCRUBBING DATA SHEET

DATE: 3-15-72

SCRUB: 31 gm of CaO plus 8 gm $CaSO_3$ in 1 litre of water plus SO_2; pH 6.4

OBJECT: NO_x scrubbing with CaO doped with $CaSO_3$.

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH 6.4 Final pH 4.7

H_2O 10 % CO_2 12 % O_2 3 %

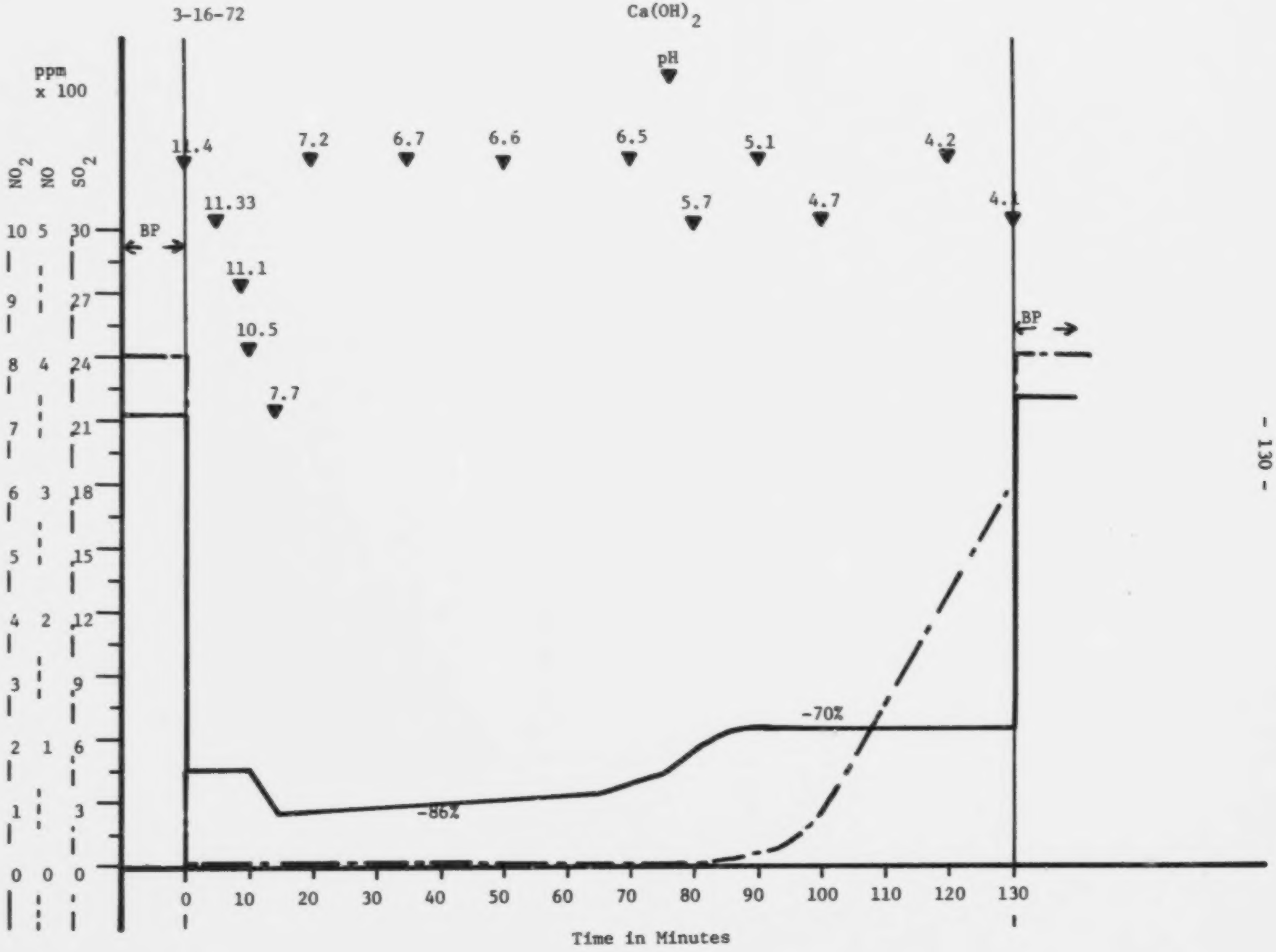
NO -- ppm NO_2 380 ppm SO_2 520 ppm

COMMENT:

(1) NO_2 was absorbed fairly constantly @ a level of 71%.

(2) The SO_2 dropped to zero and came up steadily with time and decreasing pH.

NO: $Na_2SO_3 \longrightarrow$ Dry ice $\longrightarrow$ NDIR


3-16-72
Ca(OH)$_2$
pH
ppm x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
BP
BP
11.4
11.33
11.1
10.5
7.7
7.2
6.7
6.6
6.5
5.7
5.1
4.7
4.2
4.1
-86%
-70%
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-16-72 SCRUB: $Ca(OH)_2$ [10 gm per litre of water]

OBJECT: Absorb NO_2-SO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	11.4	Final pH	4.1
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	710 ppm	SO_2	2400 ppm

COMMENT:

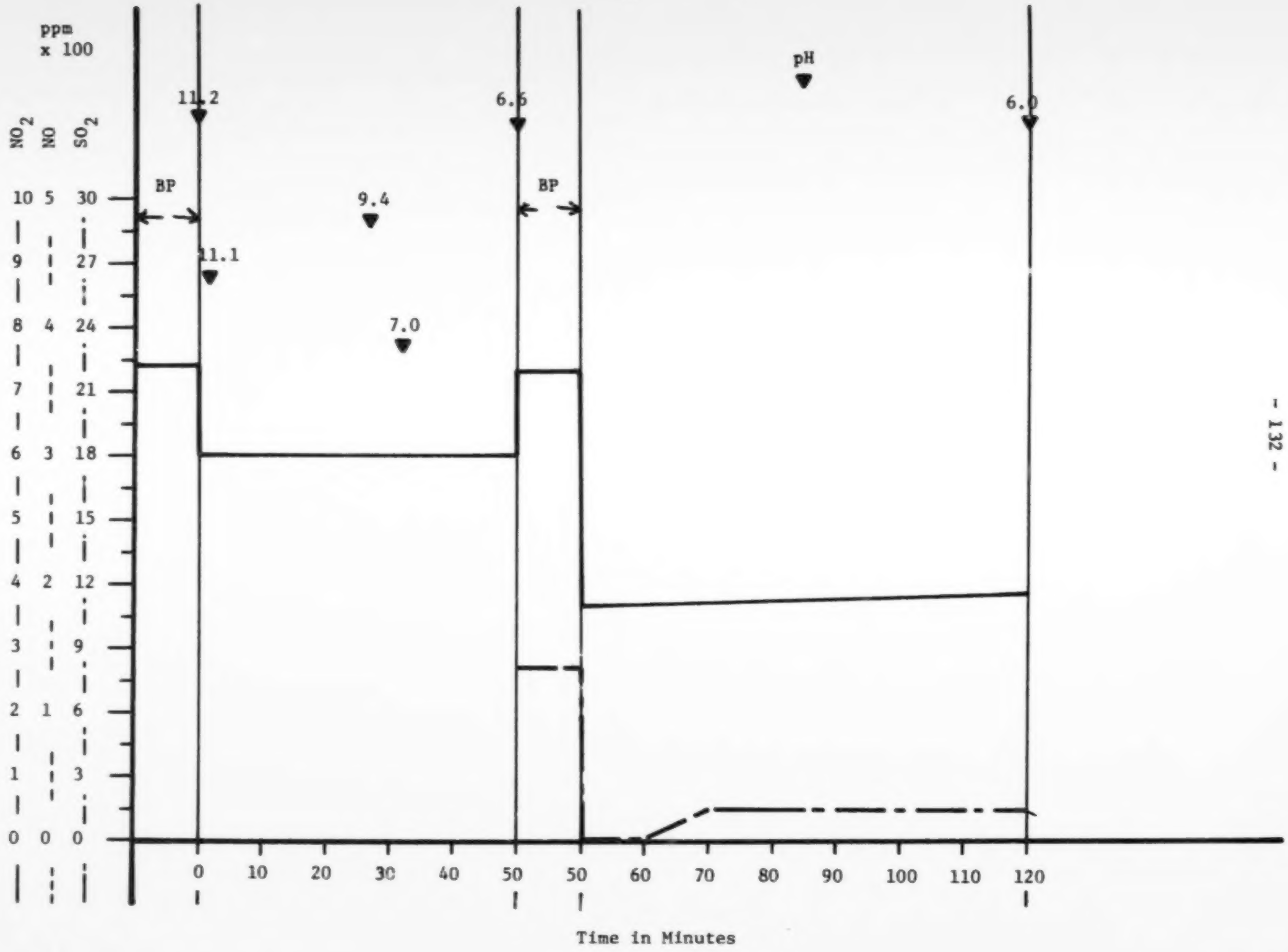
(1) After the initial pH drop, the NO_2 was absorbed to ≈86%. When the pH went under 6 → 6.5, the NO_2 absorption dropped to 70%.

(2) Initially, the SO_2 absorption was 100%. At ≈ pH 5.7 it started to drop and declined steeply below a pH of 4.7.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR

3-17-72

Ca(OH)$_2$ with an Open Tube



NOX SCRUBBING DATA SHEET

DATE: 3-17-72

SCRUB: $Ca(OH)_2$ [10 gm per litre of water]

OBJECT: Observe effect of SO2 upon NO_2 scrubbing.

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

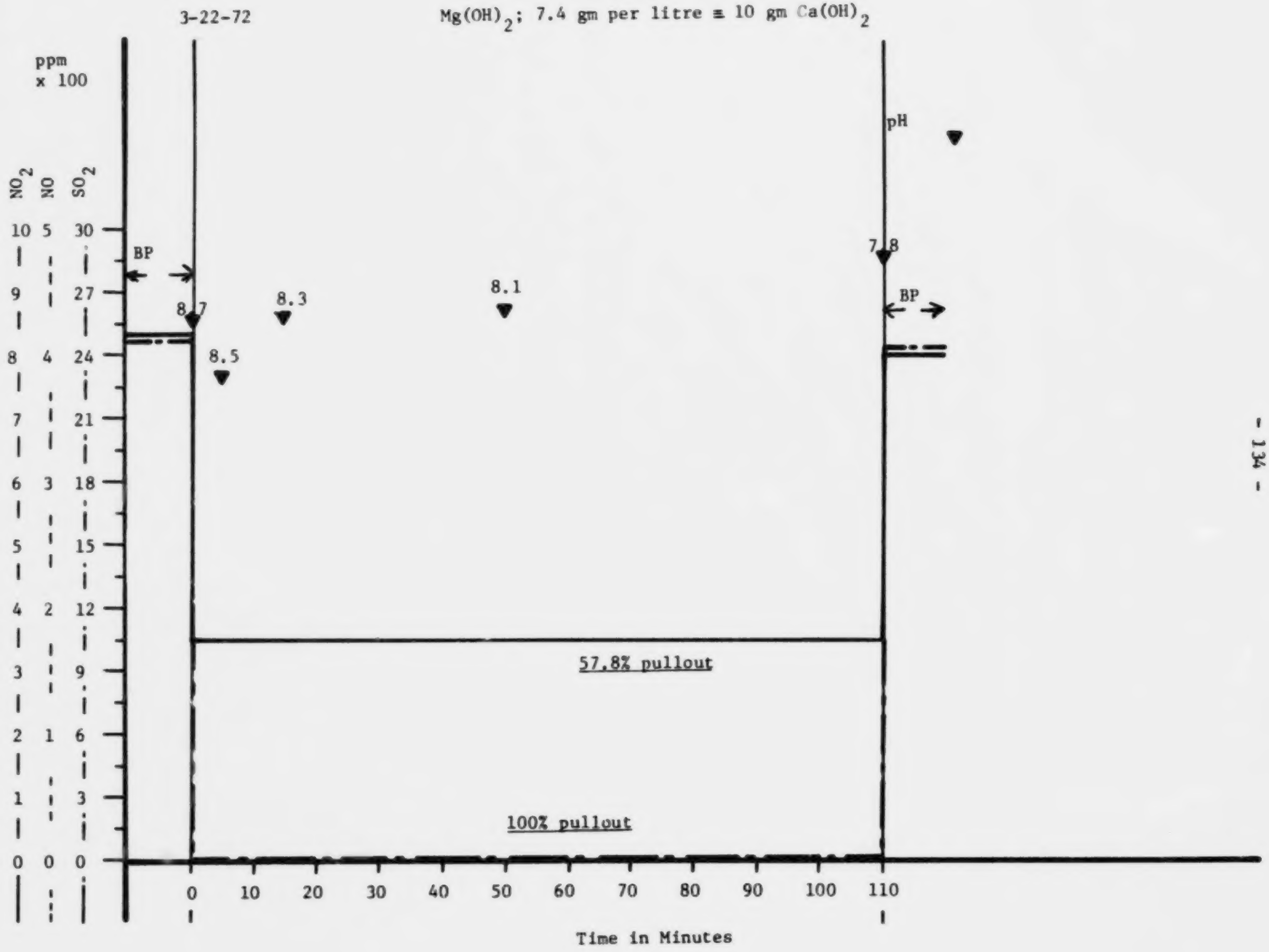
Pot Temp.	132 °F	Initial pH	11.2	Final pH	6.0
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	740 ppm	SO_2	800 ppm

COMMENT:

The presence of SO_2 significantly improved NO_2 absorption.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR

$Mg(OH)_2$; 7.4 gm per litre ≡ 10 gm $Ca(OH)_2$



NOX SCRUBBING DATA SHEET

DATE: 3-22-72 SCRUB: $Mg(OH)_2$ slurry, 7.4 gm per litre of H_2O

OBJECT: $Mg(OH)_2$ scrubbing as compared to $Ca(OH)_2$ with NO_2 - SO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

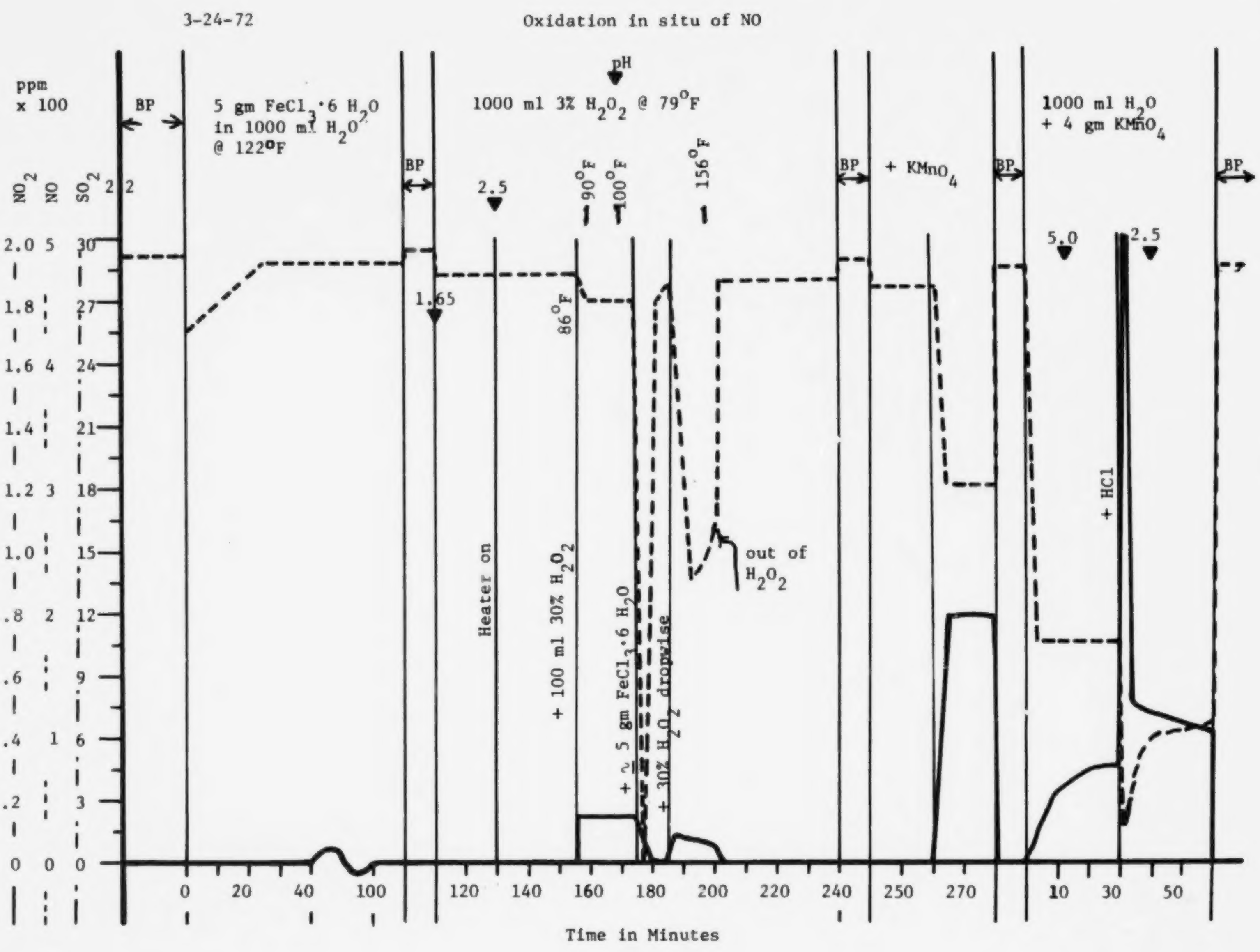
Pot Temp.	126 °F	Initial pH	8.7	Final pH	7.8
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	830 ppm	SO_2	2460 ppm

COMMENT:

(1) Absorbed 480 ppm NO_2 for the entire run. Pullout is 57.8%.

(2) Solution analyses gave 6.1 millimoles of NO_3^- and 2.0 millimoles of NO_2^- after 110 minutes.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR


3-24-72
Oxidation in situ of NO
ppm x 100
NO_2
NO
SO_2
2.0 5 30
1.8 27
1.6 4 24
1.4 21
1.2 3 18
1.0 15
.8 2 12
.6 9
.4 1 6
.2 3
0 0 0
2.2
BP
5 gm $FeCl_3 \cdot 6\ H_2O$ in 1000 ml H_2O @ 122°F
BP
1.65
2.5
Heater on
pH
1000 ml 3% H_2O_2 @ 79°F
+ 100 ml 30% H_2O_2
86°F
90°F
100°F
+ ~ 5 gm $FeCl_3 \cdot 6\ H_2O$
+ 30% H_2O_2 dropwise
156°F
out of H_2O_2
BP
+ $KMnO_4$
BP
1000 ml H_2O + 4 gm $KMnO_4$
5.0
+ HCl
2.5
BP
0
20
40
100
120
140
160
180
200
220
240
250
270
10
30
50
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-24-72 SCRUB: Water with additions

OBJECT: To absorb NO

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 485 ppm NO_2 0 ppm SO_2 NA ppm

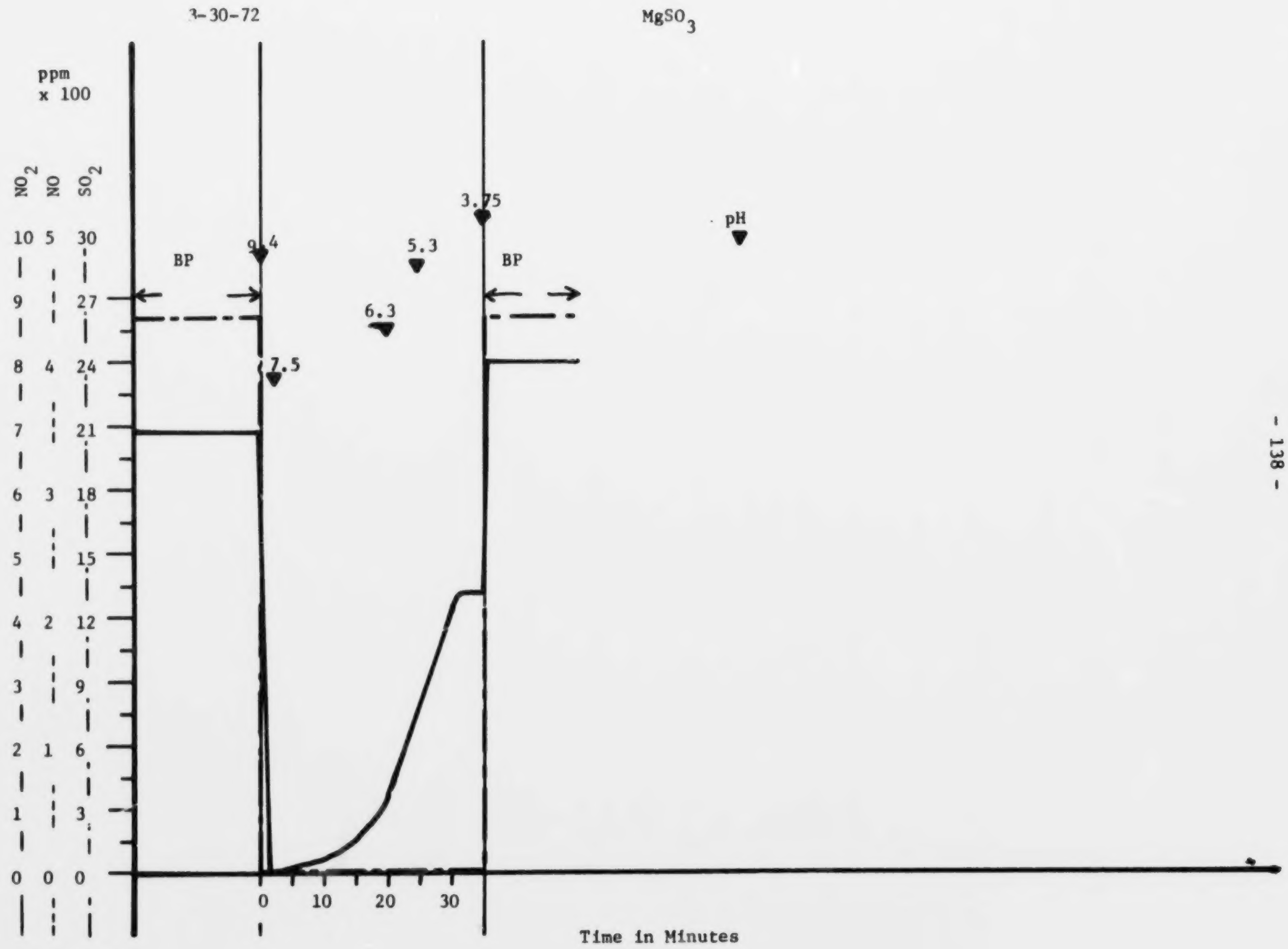
COMMENT:

(1) $FeCl_3$ is not effective. Neither is plain 3% H_2O_2.

(2) 30% H_2O_2 does work, but not well. The addition of $FeCl_3$, catalyzes the system well.

(3) The $KMnO_4$ proved best.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR


3-30-72
MgSO$_3$
ppm x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
BP
9.4
7.5
6.3
5.3
3.75
BP
pH
0
10
20
30
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 3-30-72 SCRUB: $MgSO_3$ (5 gm/1000 ml H_2O)

OBJECT: NO_2 - SO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH 9.4 Final pH 3.75

H_2O 10 % CO_2 12 % O_2 3 %

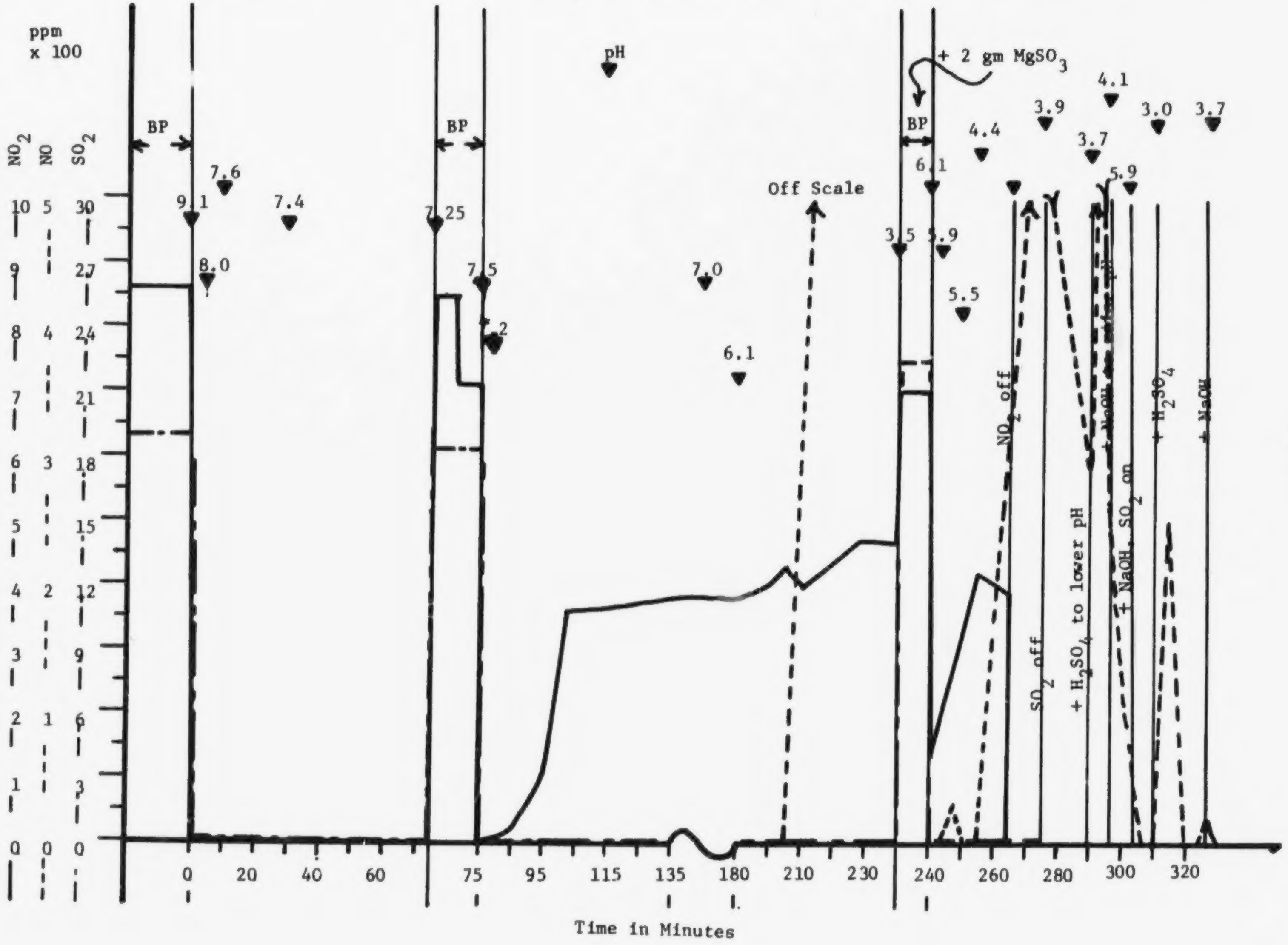
NO NA ppm NO_2 690 ppm SO_2 2610 ppm

COMMENT:

(1) NO_2 dropped quickly to zero and then increased steadily.

NO: Na_2SO_3 → Dry Ice → NDIR

CaSO$_3$ Long Term and Vary pH



NOX SCRUBBING DATA SHEET

DATE: 4-5-72 SCRUB: $CaSO_3$ (25 gm per litre of water)

OBJECT: NO_2 - SO_2 absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH 9.1 Final pH 7.25

H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 860 ppm SO_2 1890 ppm

COMMENT:

(1) The NO_2 and SO_2 were absorbed to the level of 100%.

NO: Na_2SO_3 → Dry Ice → NDIR

NOX SCRUBBING DATA SHEET

DATE: 4-5-72

SCRUB: Bath from page 1

OBJECT: Continue $CaSO_3$ scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 7.5 Final pH 3.5

H_2O 10 % CO_2 12 % O_2 3 %

NO 0 ppm NO_2 710 ppm SO_2 183 ppm

COMMENT:

(1) When pH went below ≈ 7.2, the NO_2 level increased quickly and settled down to ≈ 46% absorption.

(2) After passing ≈ pH 6.1, the pH dropped very quickly to 3.5, reducing the NO_2 scrubbing to ≈ 34% and generating an off scale "NO" reading.

NOX SCRUBBING DATA SHEET

DATE: 4-5-72

SCRUB: Bath from Page 2 with 2 gm of $MgSO_3$ added

OBJECT: pH variation with H_2SO_4 (≈ 10%) and NaOH (≈ 10%)

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH 6.1 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 0 ppm NO_2 700 ppm SO_2 2250 ppm

COMMENT:

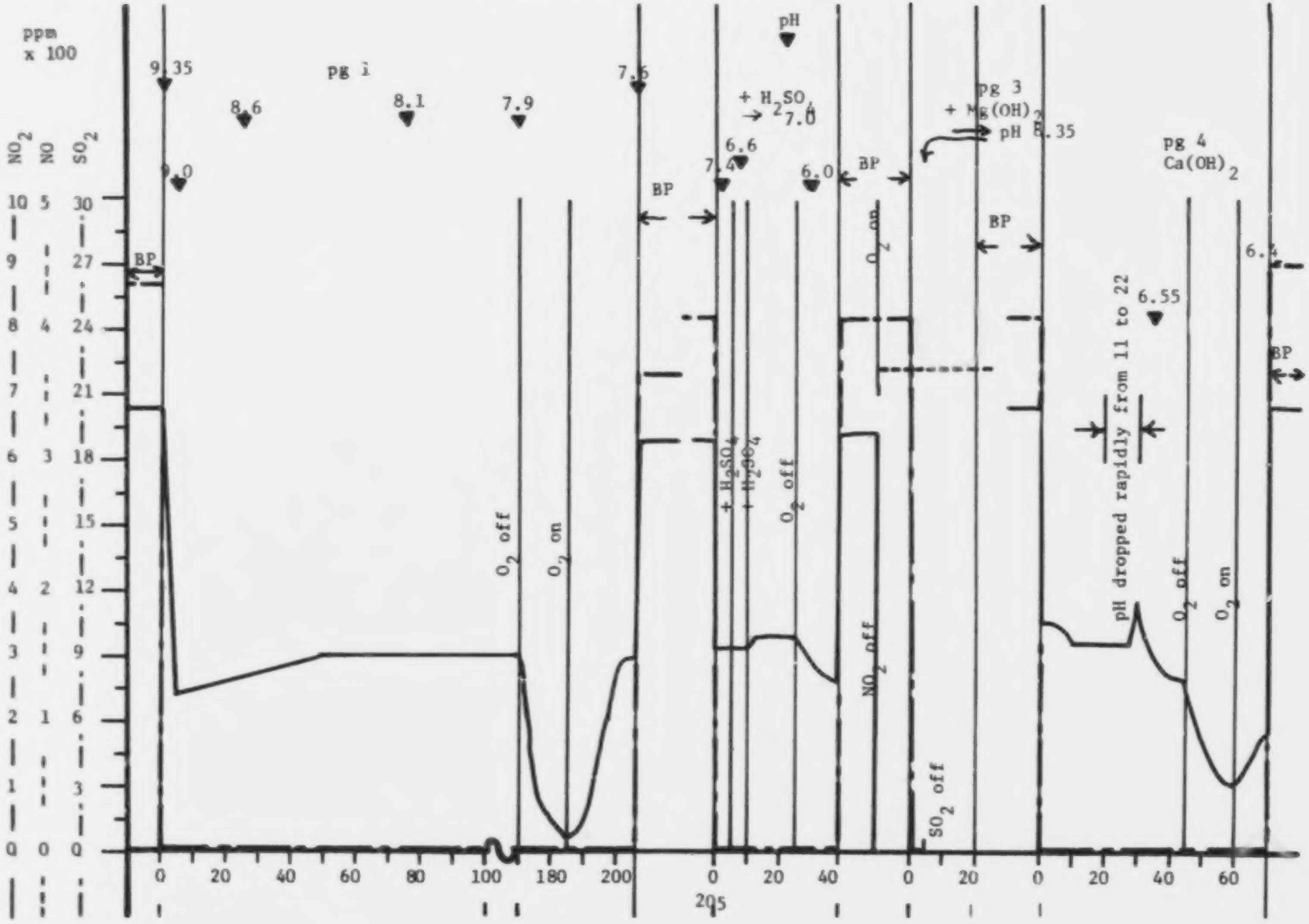
(1) After going on line, the pH quickly dropped with the NO_2 appearing to head back to the level recorded on page 2.

(2) At ≈ pH 4.4, "NO" broke through to an off-scale reading. Turning the NO_2 off did not effect it. Turning the SO_2 off immediately brought the "NO" down.

(3) With the SO_2 and NO_2 off, a decrease in pH (with H_2SO_4) causes the "NO" to again rise; increase pH with NaOH again removes the NO.

4-7-72

Comparison of $Mg(OH)_2$ and $Ca(OH)_2$



NOX SCRUBBING DATA SHEET

DATE: 4-7-72

SCRUB: $Mg(OH)_2$ and $Ca(OH)_2$

$Mg(OH)_2$ @ 14 gm/1

OBJECT: NO_2 - SO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	126 °F	Initial pH	9.35	Final pH	7.6
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	680 ppm	SO_2	2610 ppm

COMMENT:

(1) At 2610 ppm SO_2 and a total flow of 3200 cm^3/min, we would need 706 min of 100% absorption to yield $SO_3^=$ level of 25 gm of $MgSO_3$.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR

NOX SCRUBBING DATA SHEET

DATE: 4-7-72

SCRUB: $Mg(OH)_2$ from Page 1 acidified to pH 7 from 7.6 with H_2SO_4

OBJECT: NO_2 - SO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	126 °F	Initial pH	7.0	Final pH	see chart
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	630 ppm	SO_2	2460 ppm

COMMENT:

(1) Large volumes of gas were liberated with the addition of the H_2SO_4. The pH dropped rapidly and then came back up slowly.

NOX SCRUBBING DATA SHEET

DATE: 4-7-72   SCRUB: $Mg(OH)_2$ from Page 2 + more

$Mg(OH)_2 \rightarrow$ pH 8.35

OBJECT: Scrubbing NO

CONDITIONS: Scrub volume @ 1000 ml   Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F   Initial pH 8.35   Final pH ______

H_2O 10 % CO_2 12 % O_2 3 %

NO 370 ppm NO_2 NA ppm SO_2 2460 ppm

COMMENT:

(1) No NO was absorbed.

NOX SCRUBBING DATA SHEET

DATE: 4-7-72

SCRUB: $Ca(OH)_2$ [17.8 gm $Ca(OH)_2$ per 1000 ml H_2O]

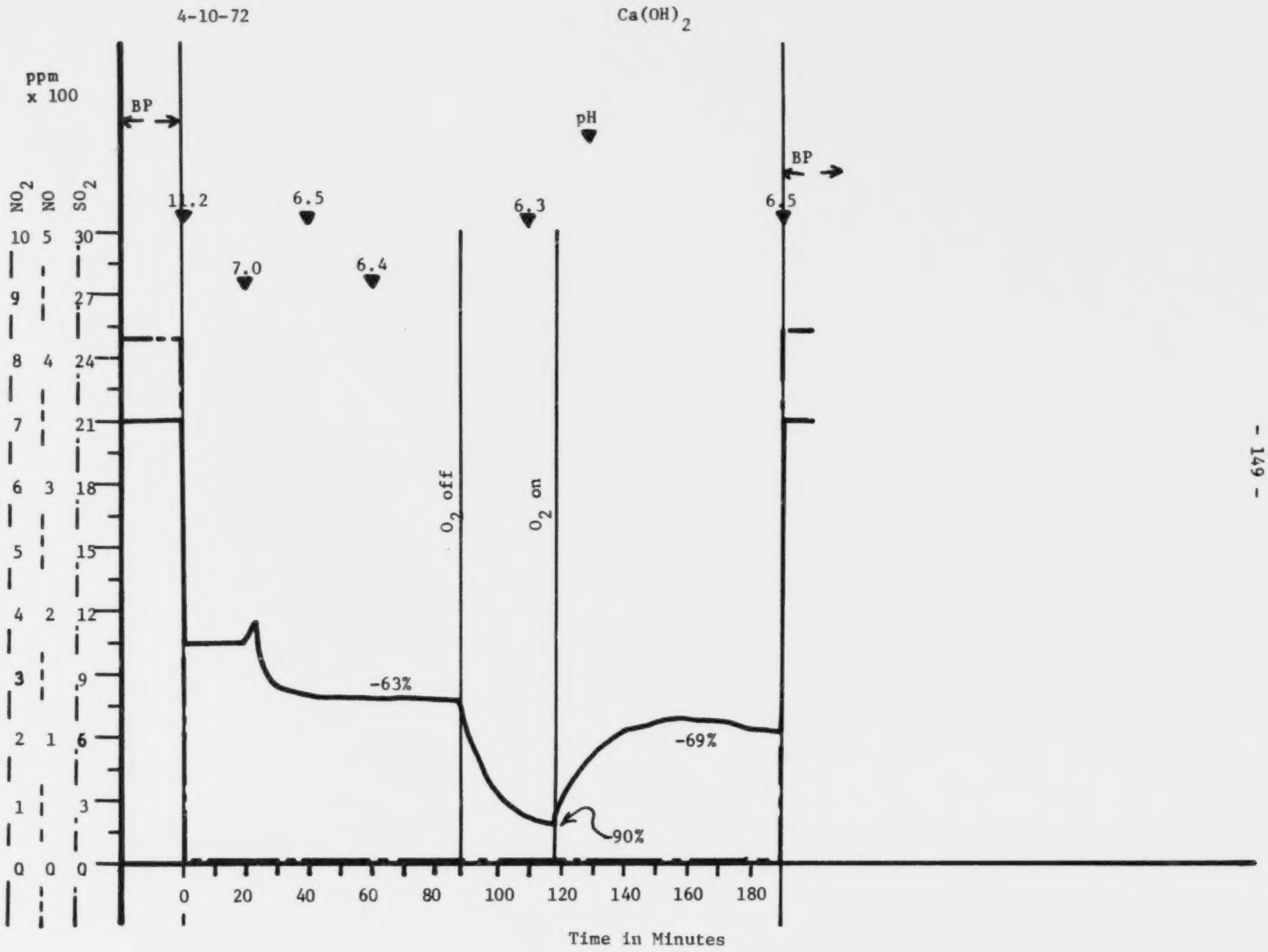
OBJECT: Comparision of Ca and Mg systems

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F	Initial pH 11.2	Final pH 6.4
H_2O 10 %	CO_2 12 %	O_2 3 %
NO NA ppm	NO_2 680 ppm	SO_2 2460 ppm

COMMENT:

(1) With oxygen present, the $Ca(OH)_2$ appears to be more efficient.


4-10-72
Ca(OH)$_2$
ppm
x 100
BP
BP
pH
NO_2
NO
SO_2
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
11.2
7.0
6.5
6.4
6.3
6.5
-63%
-69%
90%
O_2 off
O_2 on
0
20
40
60
80
100
120
140
160
180
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-10-72

SCRUB: $Ca(OH)_2$ slurry (15 gm per litre of H_2O)

OBJECT: $Ca(OH)_2$ vs. ZnO

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	126 °F	Initial pH	11.2	Final pH	6.5
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	700 ppm	SO_2	2490 ppm

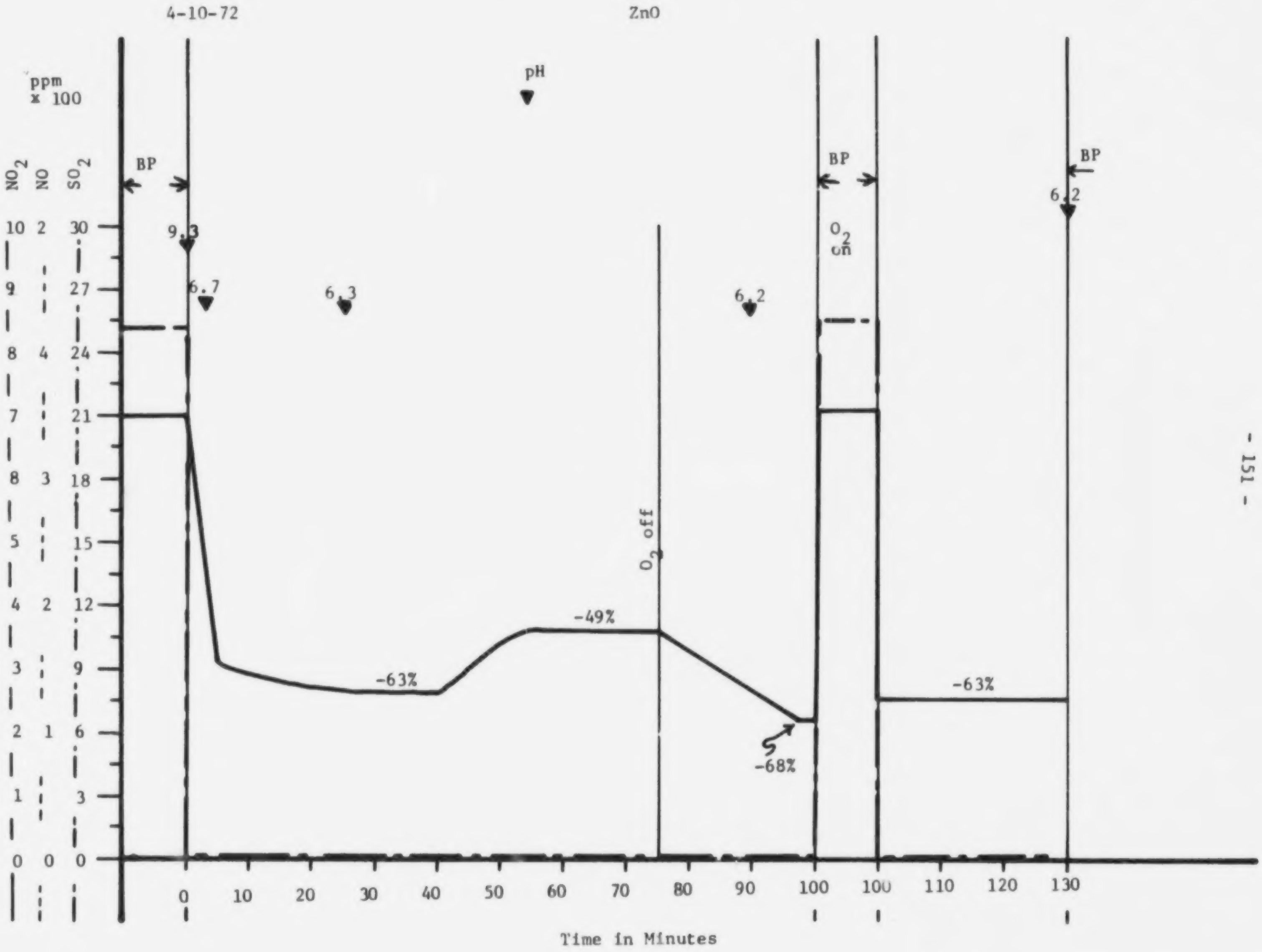
COMMENT:

(1) After the pH dropped below 7, the NO_2 absorption was 63%.

(2) Without O_2, absorption ≈ 90% and later at pH of 6.4, with O_2 back on, the absorption was ·69%.

(3) The SO_2 absorption was 100%.

NO: Na_2SO_3 → Dry Ice → NDIR


4-10-72
ZnO
ppm
x 100
NO_2
NO
SO_2
10 9 8 7 8 5 4 3 2 1 0
2 4 3 2 1 0
30 27 24 21 18 15 12 9 6 3 0
BP
BP
BP
pH
9.3
6.7
6.3
6.2
6.2
-63%
-49%
-68%
-63%
O_2 off
O_2 on
0 10 20 30 40 50 60 70 80 90 100 100 110 120 130
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-10-72 SCRUB: ZnO slurry (10 gm per litre water)

OBJECT: Ca(OH)2 vs. ZnO

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	126 °F	Initial pH	9.3	Final pH	6.2
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	700 ppm	SO_2	2520 ppm

COMMENT:

(1) NO_2 pullout was initially ≈ 63%.

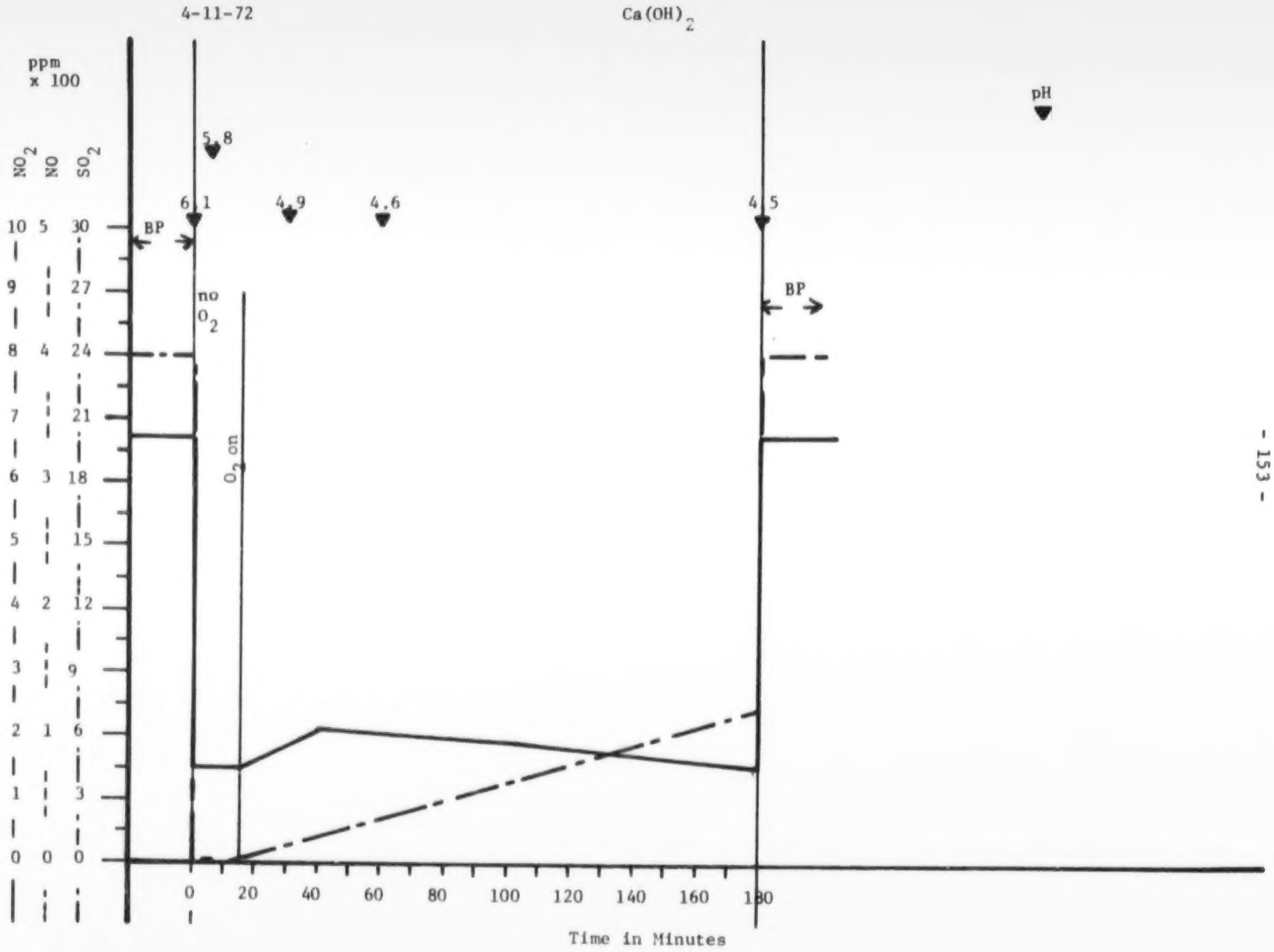
(2) This dropped to 49% with lower pH (6.2).

(3) With the O_2 off, 68% of NO_2 absorbed.

(4) Back on with O_2, 63% NO_2 absorbed.

(5) SO_2 absorption was always 100%.

NO: $Na_2SO_3 \longrightarrow$ dry ice $\longrightarrow$ NDIR


4-11-72
Ca(OH)$_2$
ppm
x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
pH
5.8
6.1
4.9
4.6
4.5
BP
no O$_2$
O$_2$ on
BP
0
20
40
60
80
100
120
140
160
180
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-11-72

SCRUB: $Ca(OH)_2$ slurry pre-doped with SO_2; 15 gm/1000 ml H_2O

OBJECT: To test $Ca(OH)_2$ lower pH and high $SO_3^{=}$

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

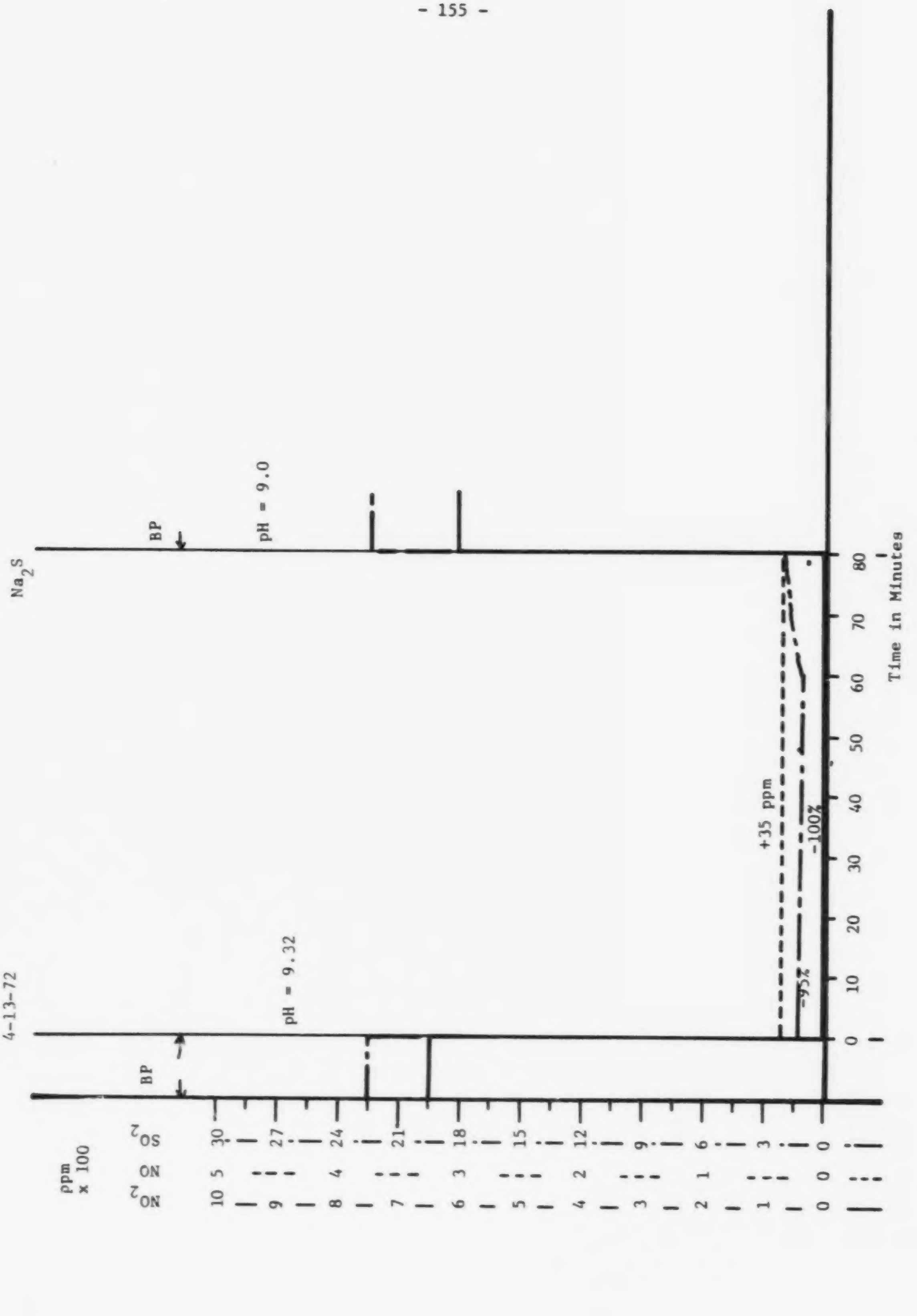
Pot Temp.	124 °F	Initial pH	6.1	Final pH	4.5
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	670 ppm	SO_2	2400 ppm

COMMENT:

(1) The slurry of $Ca(OH)_2$ (15 gm/1000 ml H_2O) was stirred, and through it bubbled an SO_2-N_2 mixture until the pH was between 6 and 7.

(2) NO_2 scrubbing was on a par with former runs. The SO_2 broke through early and rose steadily.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR


4-13-72
Na_2S
BP
pH = 9.32
pH = 9.0
BP
+35 ppm
-95%
-100%
Time in Minutes
0
10
20
30
40
50
60
70
80
ppm x 100
NO_2 0 1 2 3 4 5 6 7 8 9 10
NO 0 1 2 3 4 5
SO_2 0 3 6 9 12 15 18 21 24 27 30

NOX SCRUBBING DATA SHEET

DATE: 4-13-72 SCRUB: 1.88 molal Na_2S

OBJECT: NO_2-SO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 131 °F Initial pH 9.32 Final pH 9.0

H_2O 8-10 % CO_2 12 % O_2 3 %

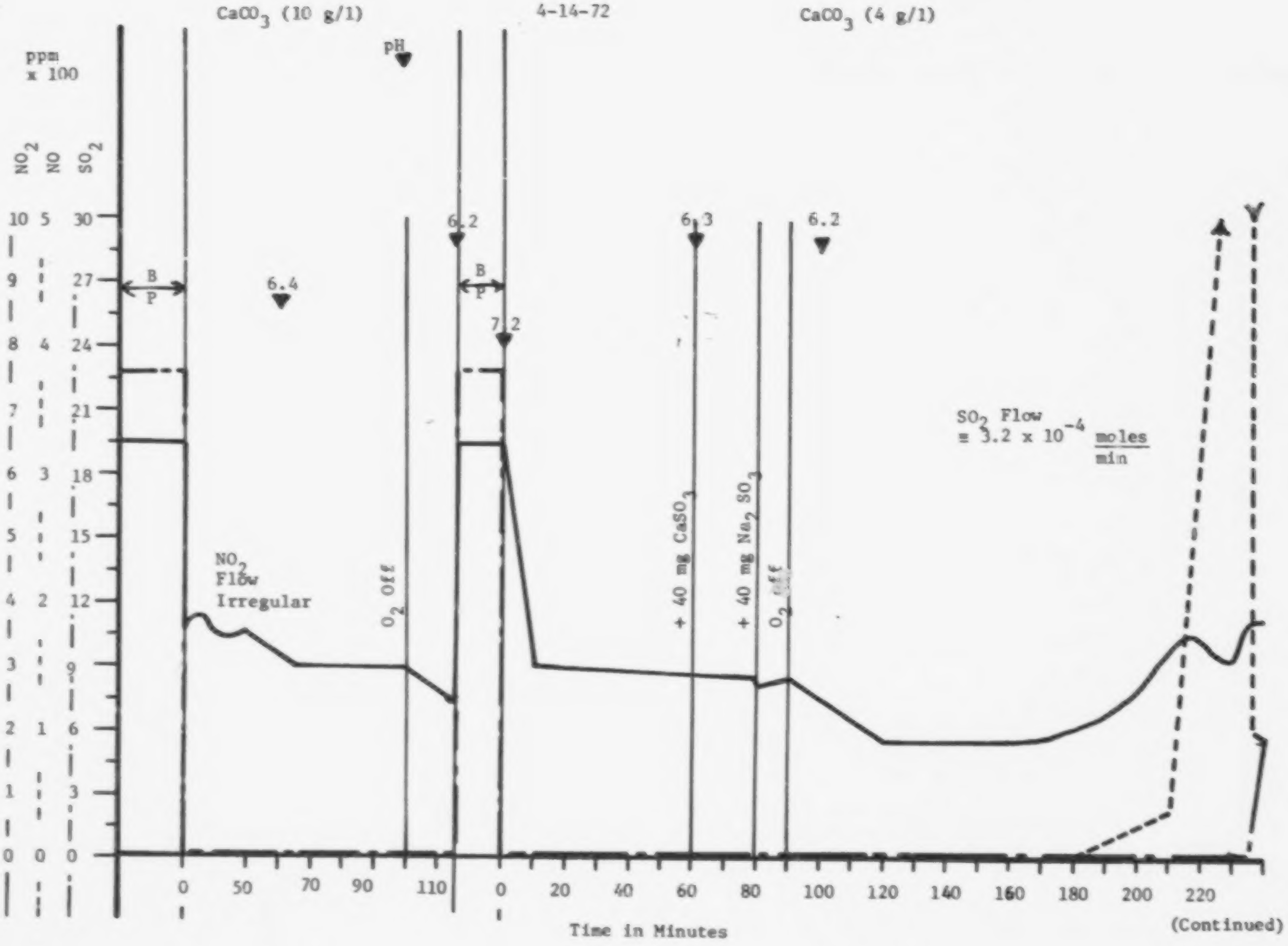
NO 0 ppm NO_2 650 ppm SO_2 2250 ppm

COMMENT:

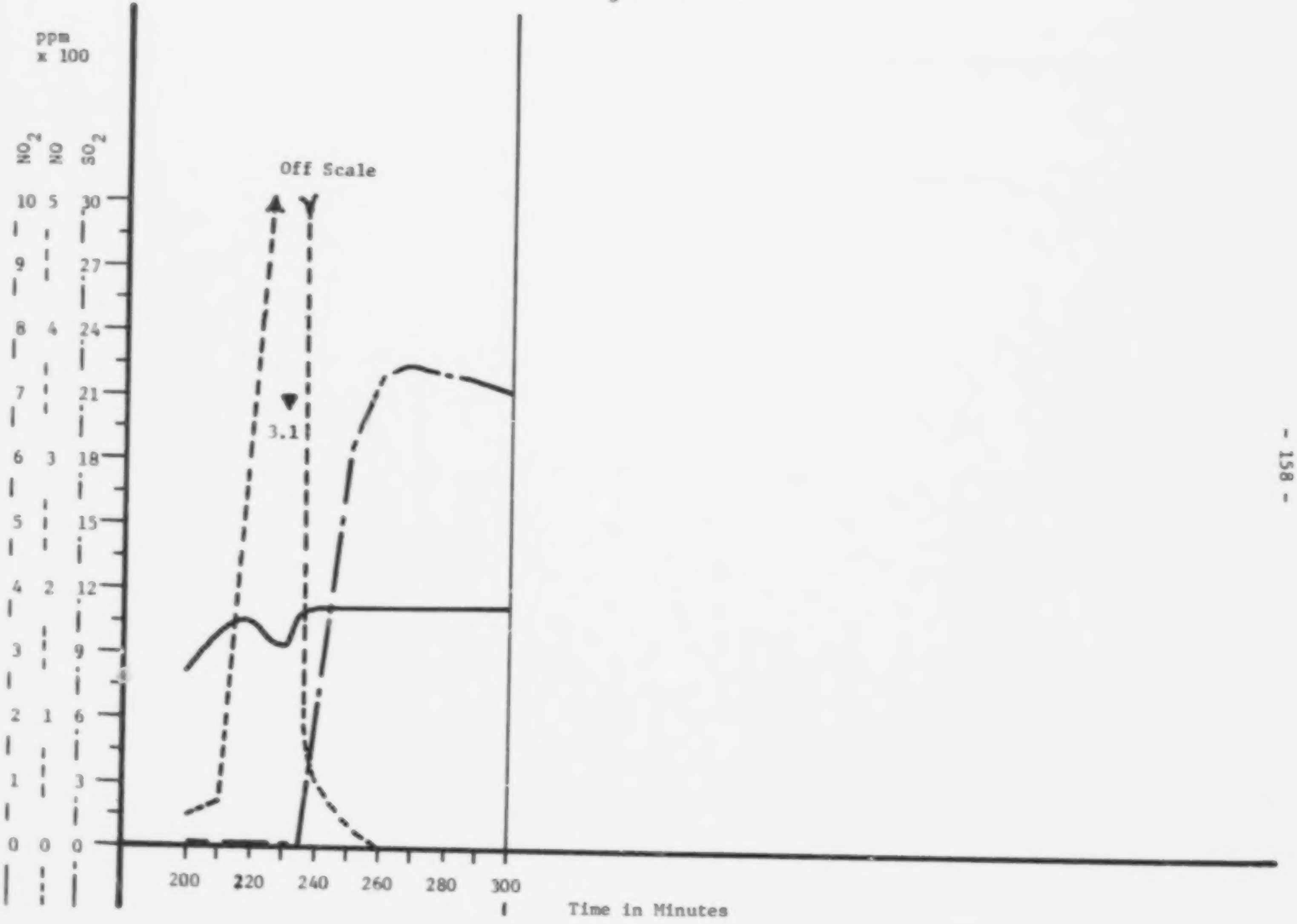
(1) The SO_2 absorption was 95% and for NO_2 was 100%. Also generated 35 ppm NO.

(2) Also generated H_2S.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR


CaCO$_3$ (10 g/1)
4-14-72
CaCO$_3$ (4 g/1)
ppm
x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
B
P
pH
6.4
6.2
7.2
6.3
6.2
NO$_2$
Flow
Irregular
O$_2$ Off
+ 40 mg CaSO$_3$
+ 40 mg Na$_2$ SO$_3$
O$_2$ off
SO$_2$ Flow
= 3.2 x 10^{-4} $\frac{\text{moles}}{\text{min}}$
0
50
70
90
110
0
20
40
60
80
100
120
140
160
180
200
220
Time in Minutes

(Continued)


CaCO$_3$ (Continued)

NOX SCRUBBING DATA SHEET

DATE: 4-13-72 / 4-14-72

SCRUB: $CaCO_3$, 10 gm in 1000 ml H_2O

OBJECT: Calcium Carbonate Scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 128 °F Initial pH 7.5 Final pH 6.2

H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 650 ppm SO_2 2280 ppm

COMMENT:

The flow slowly degraded during the run (frit was clogged) and the results are therefore inconclusive. The run was continued on 4-14-72 after being run for 50 minutes.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR

NOX SCRUBBING DATA SHEET

DATE: 4-14-72 SCRUB: $CaCO_3$ from 4-13-72

OBJECT: $CaCO_3$ Scrubbing

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 128 °F Initial pH >7 Final pH 6.2

H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 650 ppm SO_2 2280 ppm

COMMENT:

(1) Scrubbing of NO_2 improved when O_2 was removed from flue gas.

NOX SCRUBBING DATA SHEET

DATE: 4-14-72

SCRUB: $CaCO_3$, 4 gm in 1000 ml H_2O

OBJECT: NO_2-SO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	128 °F	Initial pH	7.2	Final pH	3.1
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	650 ppm	SO_2	2280 ppm

COMMENT:

(1) The addition of 40 mg ($\approx 3.3 \times 10^{-4}$ moles) of $CaSO_3$ at 60 min had no effect.

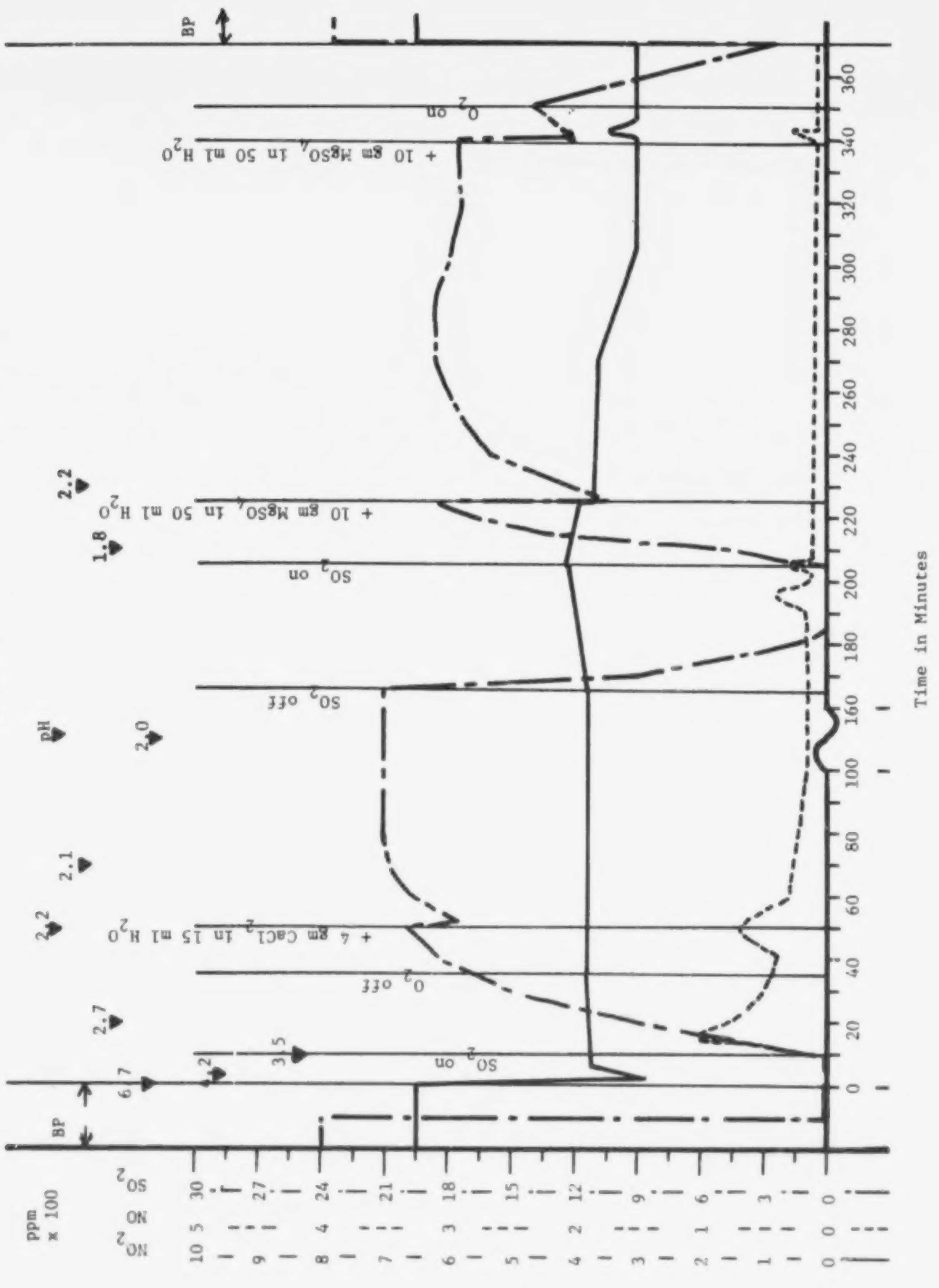
(2) At 80 min, the addition of 40 mg Na_2SO_3 had a momentary effect of reducing NO_2 by 10 ppm.

(3) The elimination of O_2 caused a decline in the NO_2 level that slowly rose again as the pH dropped.

(4) At a very low pH ($\approx$ 3.1) the SO_2 broke through to about the bypass value and then started dropping off again. At the same time, a surge of NO was generated.

H_2O with Plus Product Salts

4-17-72



NOX SCRUBBING DATA SHEET

DATE: 4-17-72 SCRUB: 1000 ml H_2O with salts added at time intervals

OBJECT: To check the scrubbing of water and various product salts

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 6.7 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 0 ppm NO_2 650 ppm SO_2 2400 ppm

COMMENT:

(1) NO_2 pullout, with or without O_2 but with SO_2 is ≈ 42%.

(2) SO_2 pullout with or without O_2 and with or without $CaCl_2$ is ≈ 13%.

(3) The $CaCl_2$ does not seem to effect the NO_2 pullout.

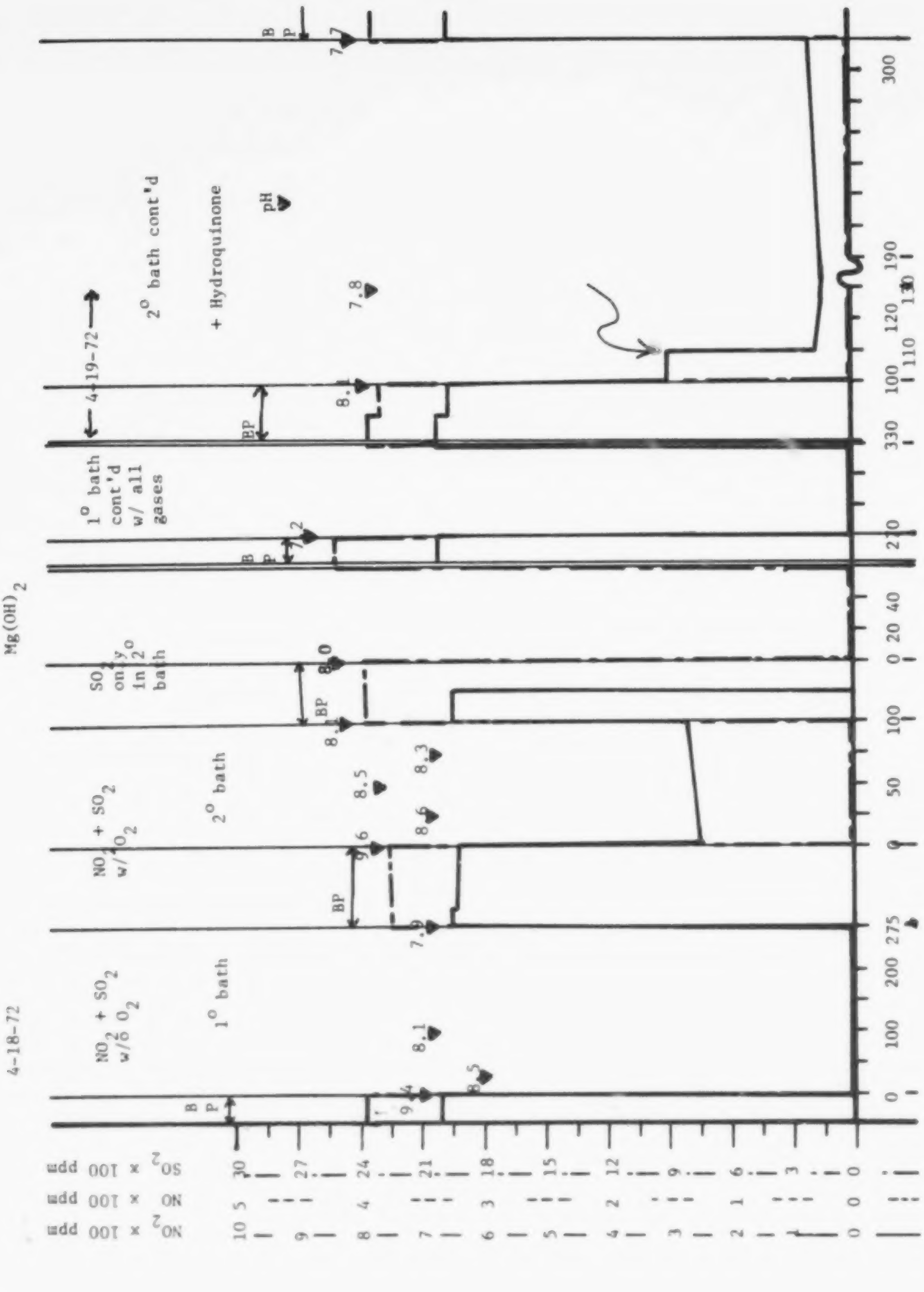
(4) Without SO_2, the NO_2 level slowly rises, though not very much (≈ 40 ppm in 40 min).

(5) Without O_2 and with $MgSO_4$; SO_2 pullout is -23%, and NO_2 ≈ 46%.

(6) With O_2 on and with $MgSO_4$, SO_2 level decreases to zero (100%) and the NO_2 seems unchanged.

(7) At an absorption of 280 ppm NO_2 (1st 10 min) and 3200 cm^3/min of gas, using $4NO_2 + 2H_2O \rightarrow 2HNO_3 + 2HNO_2$ the theoretical pH is 3.44, (3.5 was measured) assuming total ionization.

NO: Na_2SO_3 → Dry Ice → NDIR


4-18-72
$NO_2 + SO_2$ w/o O_2
1° bath
$NO_2 + SO_2$ w/ O_2
2° bath
SO_2 only in 2° bath
$Mg(OH)_2$
1° bath cont'd w/ all gases
4-19-72
2° bath cont'd
+ Hydroquinone
pH
BP
9.4
8.5
8.1
7.9
9.6
8.6
8.5
8.3
8.1
8.0
7.2
8.1
7.8
7.7
NO_2 × 100 ppm
NO × 100 ppm
SO_2 × 100 ppm
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
0
100
200
275
0
50
100
0
20
40
210
330
100
110
120
130
190
300
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-18-72 SCRUB: $Mg(OH)_2$ slurry 15 gm/1000 cm^3 of H_2O

OBJECT: Observe effect of oxygen

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F Initial pH 9.4 Final pH 7.9

H_2O 10 % CO_2 12 % O_2 0 %

NO NA ppm NO_2 670 ppm SO_2 2370 ppm

COMMENT:

(1) Both the NO_2 and SO_2 dropped to zero and remained so for the 270 minutes of run time.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR

Calibration filter in SO_2 analyzer indicated improper readout. SO_2 value in question, is probably much higher.

NOX SCRUBBING DATA SHEET

DATE: 4-18-72 SCRUB: $Mg(OH)_2$ 15 gm/1000 cm^3 H_2O

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 9.6 Final pH 8.1

H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 640 ppm SO_2 2250 ppm

COMMENT:

(1) NO_2 dropped rapidly to ≈ 250 ppm and then rose slowly to 275 ppm.

(2) All the SO_2 was absorbed.

NOX SCRUBBING DATA SHEET

DATE: 4-18-72 SCRUB: $Mg(OH)_2$, 15 gm/1000 cm^3 of H_2O

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	8.0	Final pH	8.0
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	NA ppm	SO_2	2370 ppm

COMMENT:

(1) All the SO_2 was absorbed.

(2) The bath came back to a pH of 9.3 when allowed to stand over-night (@ 20°C).

NOX SCRUBBING DATA SHEET

DATE: 4-18-72

SCRUB: $Mg(OH)_2$, 15 gm in 1000 ml H_2O; both from initial runs

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F

Initial pH 7.2

Final pH 6.95

H_2O 10 %

CO_2 12 %

O_2 3 %

NO NA ppm

NO_2 670 ppm

SO_2 2490 ppm

COMMENT:

(1) pH at 7.2 after 20 minutes at thermal equilibrium and no gas flow.

NOX SCRUBBING DATA SHEET

DATE: 4-18-72

SCRUB: Mg(OH)$_2$

OBJECT: Scrub NO_2 - SO_2 in presence of Hydroquinone (1.0 gram)

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 8.1 Final pH 7.7

H_2O 10 % CO_2 12 % O_2 3 %

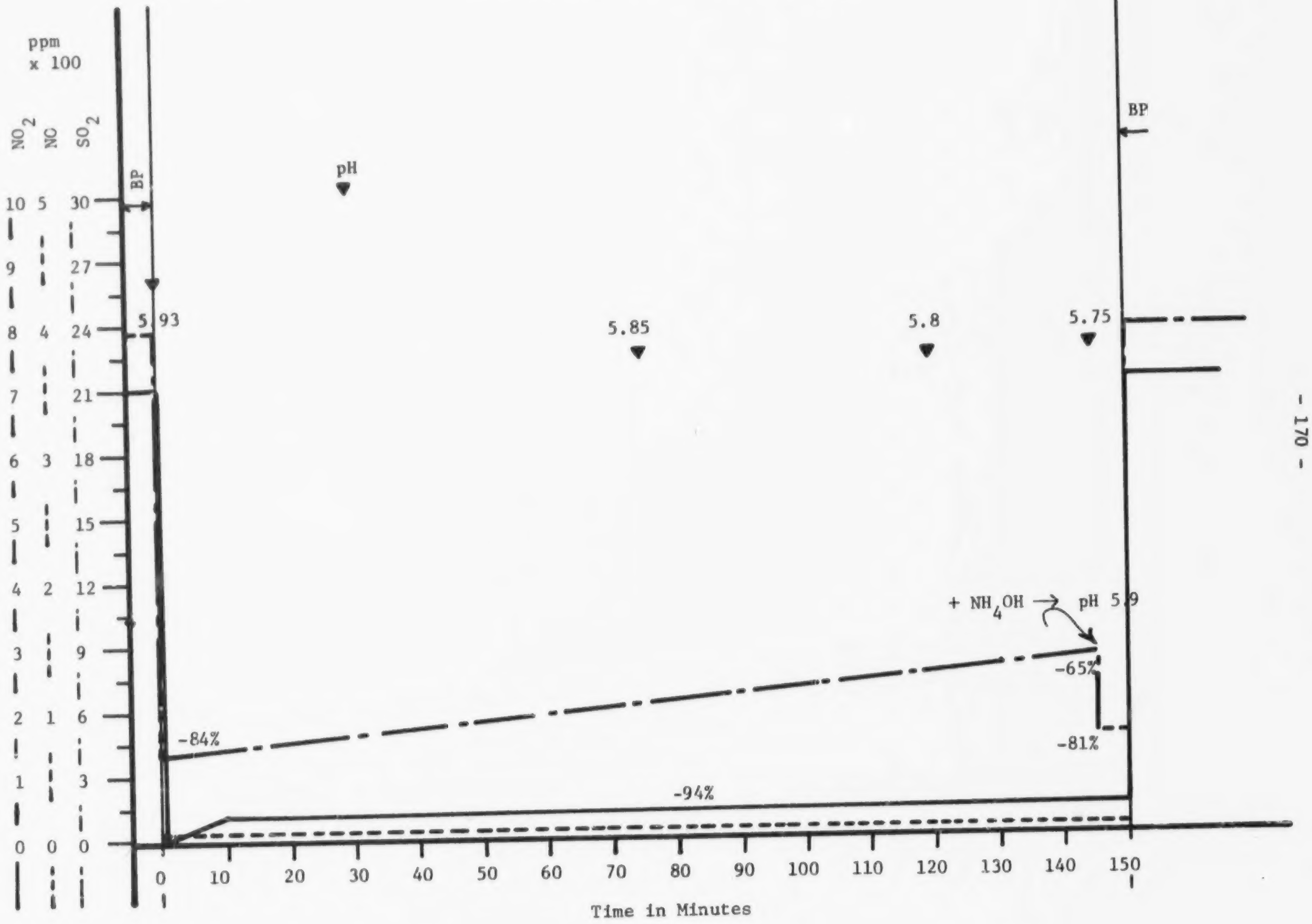
NO NA ppm NO_2 650 ppm SO_2 2280 ppm

COMMENT:

(1) Addition of HQ increased NO_2 absorption by ≈ 250 ppm.

4-24-72

2 Molal NH_4HSO_3, 0.5 Molal $(NH_4)_2SO_4$



NOX SCRUBBING DATA SHEET

DATE: 4-24-72

SCRUB: 2 molal NH_4HSO_3 with 0.5 molal $(NH_4)_2SO_4$

OBJECT: Maintain pH of solution.

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 5.93 Final pH 5.9

H_2O 10 % CO_2 12 % O_2 3 %

NO -- ppm NO_2 700 ppm SO_2 2370 ppm

COMMENT:

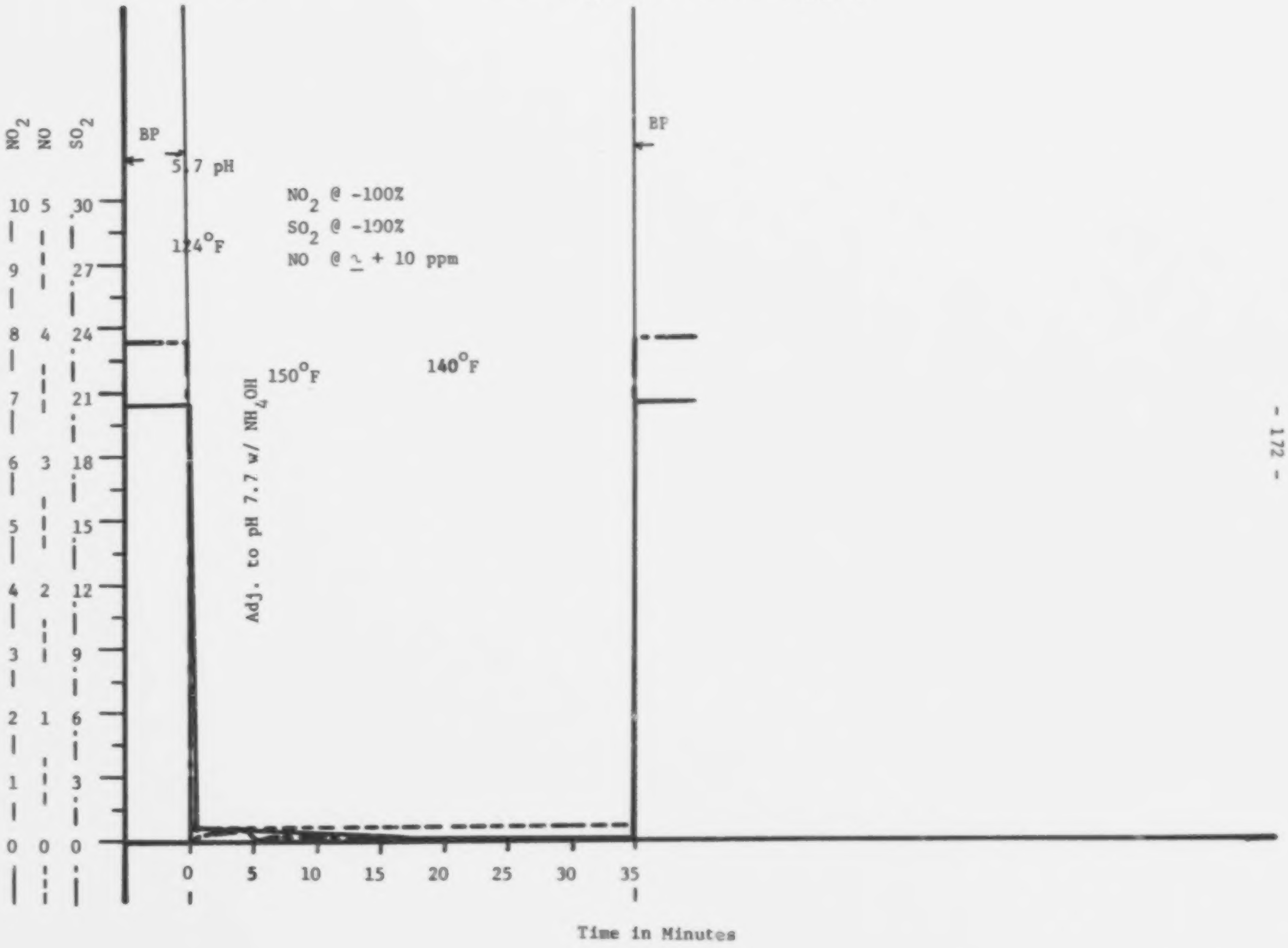
(1) The SO_2/absorption decreased steadily through the run from 84% initially to 65% at 145 min. The addition of base (NH_4OH) at 145 min, increased pullout to 81% at pH of 5.9.

(2) NO_2 pullout was ≈ 94%.

(3) It appeared that some NO was made, but within the sensitivity of the instrument, it is not possible to say exactly how much. Approximately 5-10 ppm is the best estimate.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR

4-25-72 2 Molal NH_4HSO_3, 0.5 Molal $(NH_4)_2SO_4$



NOX SCRUBBING DATA SHEET

DATE: 4-25-72 SCRUB: 2 molal NH_4HSO_3 + 0.5 molal $(NH_4)_2SO_4$

OBJECT: Observe effect of increased pH on solution used in run 4-24-72

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F Initial pH 7.7 Final pH ______

H_2O 10 % CO_2 12 % O_2 3 %

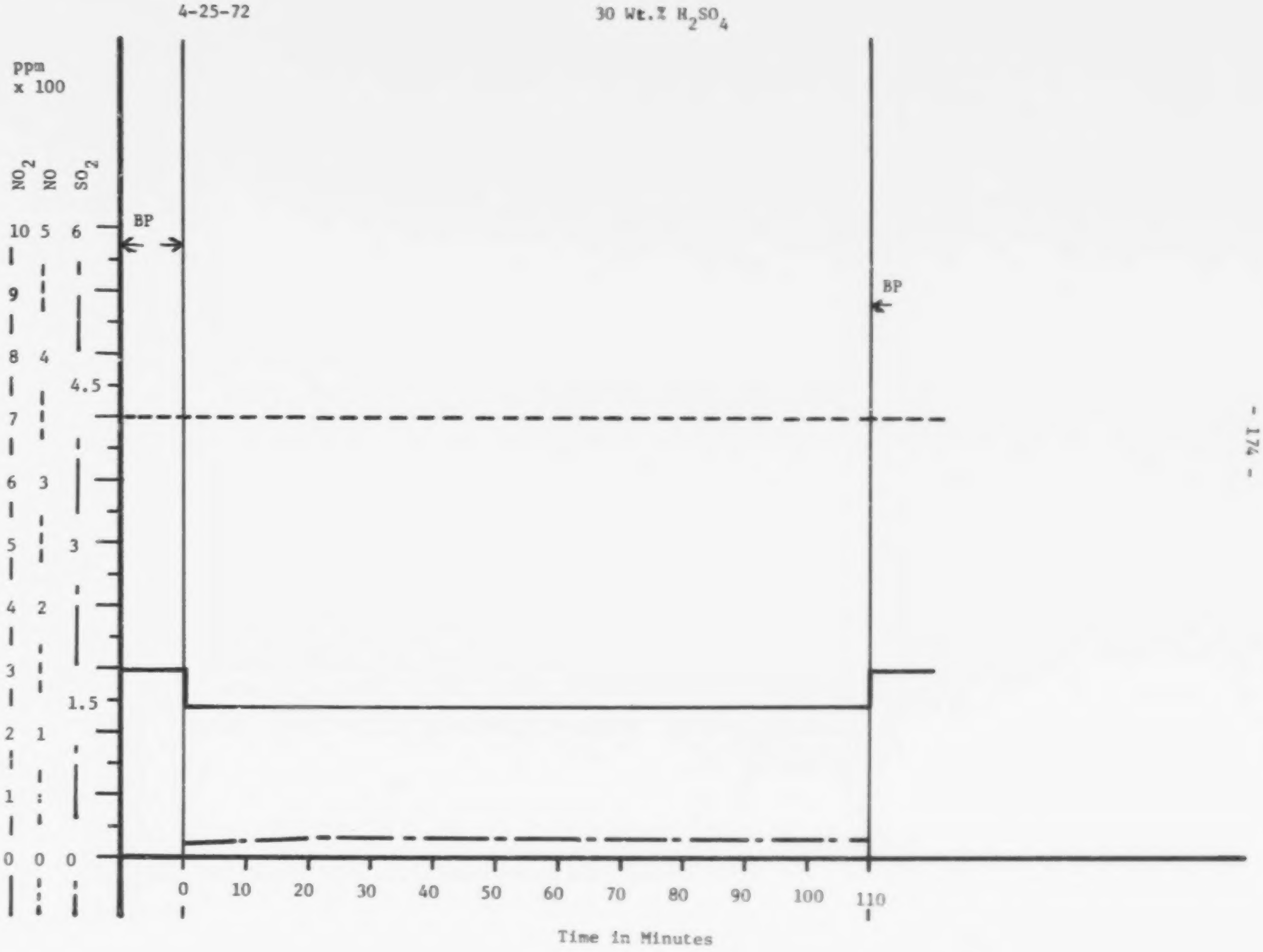
NO -- ppm NO_2 680 ppm SO_2 2340 ppm

COMMENT:

(1) SO_2 and NO_2 levels decreased after adding NH_4OH; ΔSO_2 and ΔNO_2 are 100% with 10 ppm NO generated.

(2) Solution temperature rise due to heat of neutralization.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR


4-25-72
30 Wt.% H_2SO_4
ppm
x 100
NO_2
NO
SO_2
10 5 6
9
8 4
4.5
7
6 3
5 3
4 2
3
1.5
2 1
1
0 0 0
BP
BP
0
10
20
30
40
50
60
70
80
90
100
110
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-25-72 SCRUB: H_2SO_4 30 wt. % in water

OBJECT: NO_x scrubbing with H_2SO_4

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 120 °F Initial pH -- Final pH --

H_2O 10 % CO_2 12 % O_2 3 %

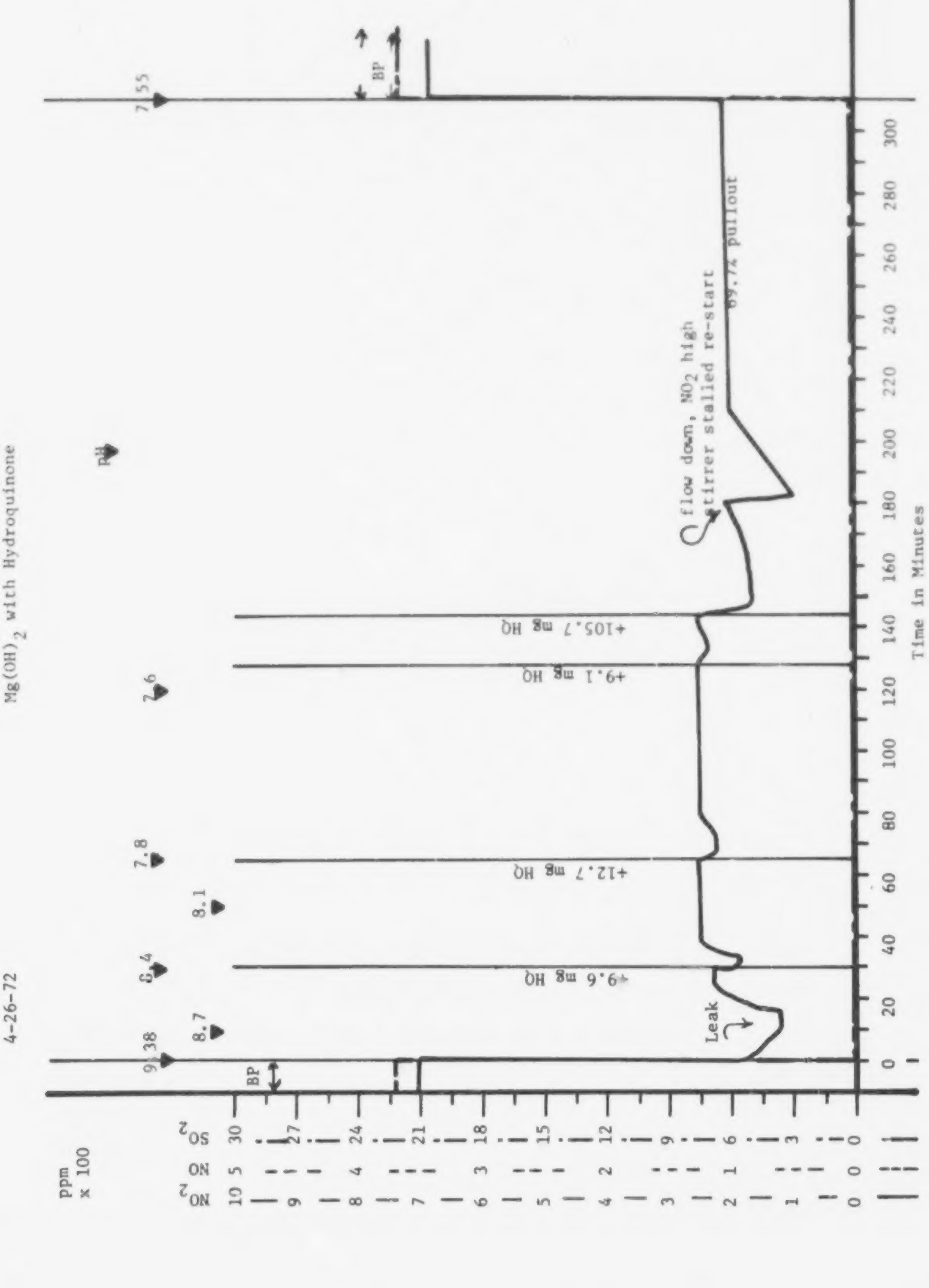
NO 350 ppm NO_2 300 ppm SO_2 0 ppm

COMMENT:

(1) No NO was absorbed.

(2) Some NO_2 (≈ 50 ppm) was absorbed and approximately 18 ppm of SO_2 was generated.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR


4-26-72
Mg(OH)$_2$ with Hydroquinone
ppm
x 100
NO$_2$ 10 9 8 7 6 5 4 3 2 1 0
NO 5 4 3 2 1 0
SO$_2$ 30 27 24 21 18 15 12 9 6 3 0
BP
9.38
8.7
8.4
8.1
7.8
7.6
7.55
pH
Leak
+9.6 mg HQ
+12.7 mg HQ
+9.1 mg HQ
+105.7 mg HQ
flow down, NO$_2$ high
stirrer stalled re-start
89.7% pullout
BP
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-26-72 SCRUB: $Mg(OH)_2$ slurry, 15 gm per litre H_2O

OBJECT: Add various amounts of Hydroquinone

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 9.38 Final pH 7.55

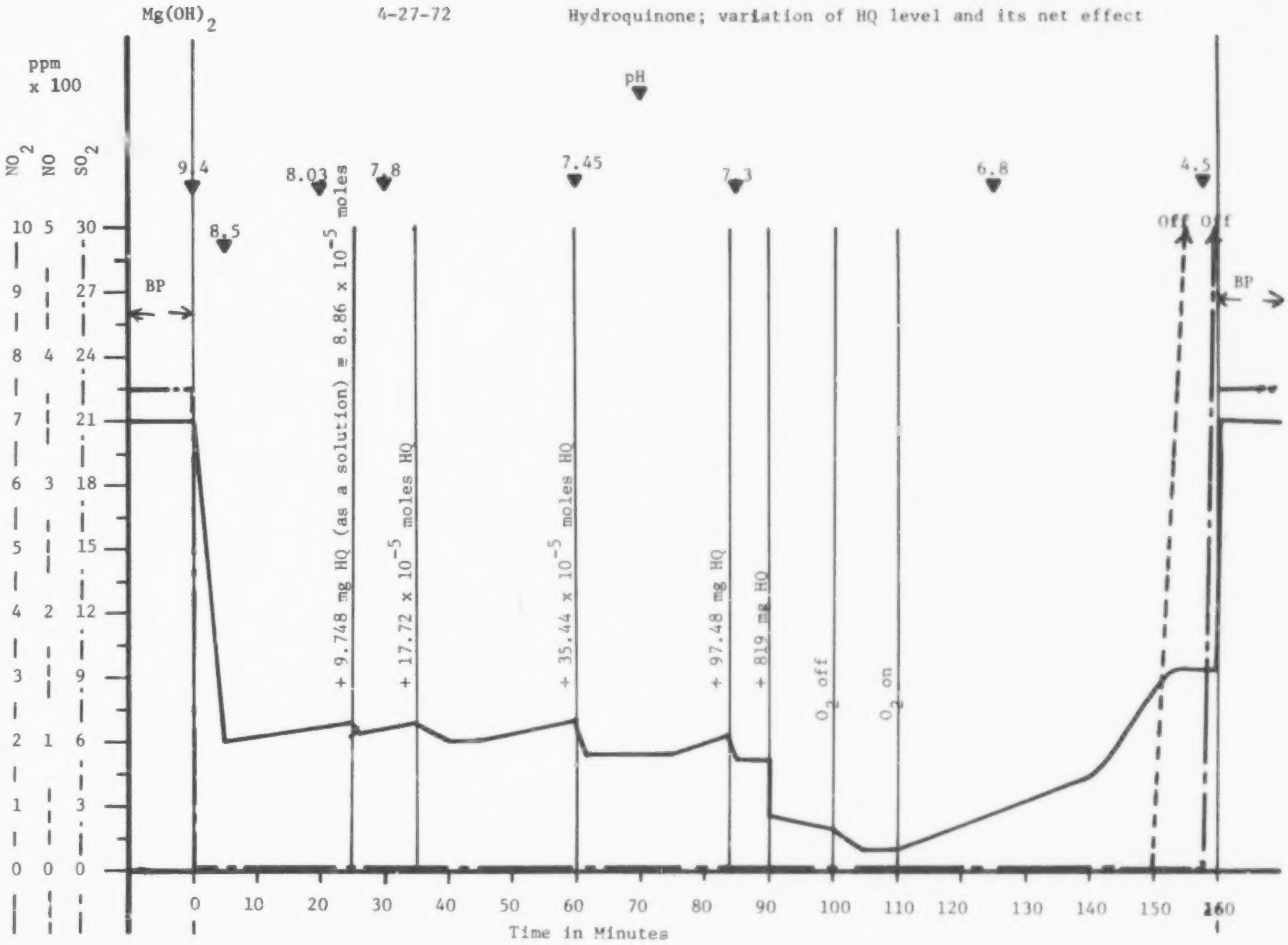
H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 705 ppm SO_2 2220 ppm

COMMENT:

(i) Final NO_2 removal was ≈ 70%, SO_2 absorption was 100%.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR



Hydroquinone; variation of HQ level and its net effect

NOX SCRUBBING DATA SHEET

DATE: 4-27-72 SCRUB: $Mg(OH)_2$ slurry, 3 gm in 1000 ml of H_2O

OBJECT: Hydroquinone testing as an anti-oxidant

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 126 °F Initial pH 9.4 Final pH 4.5

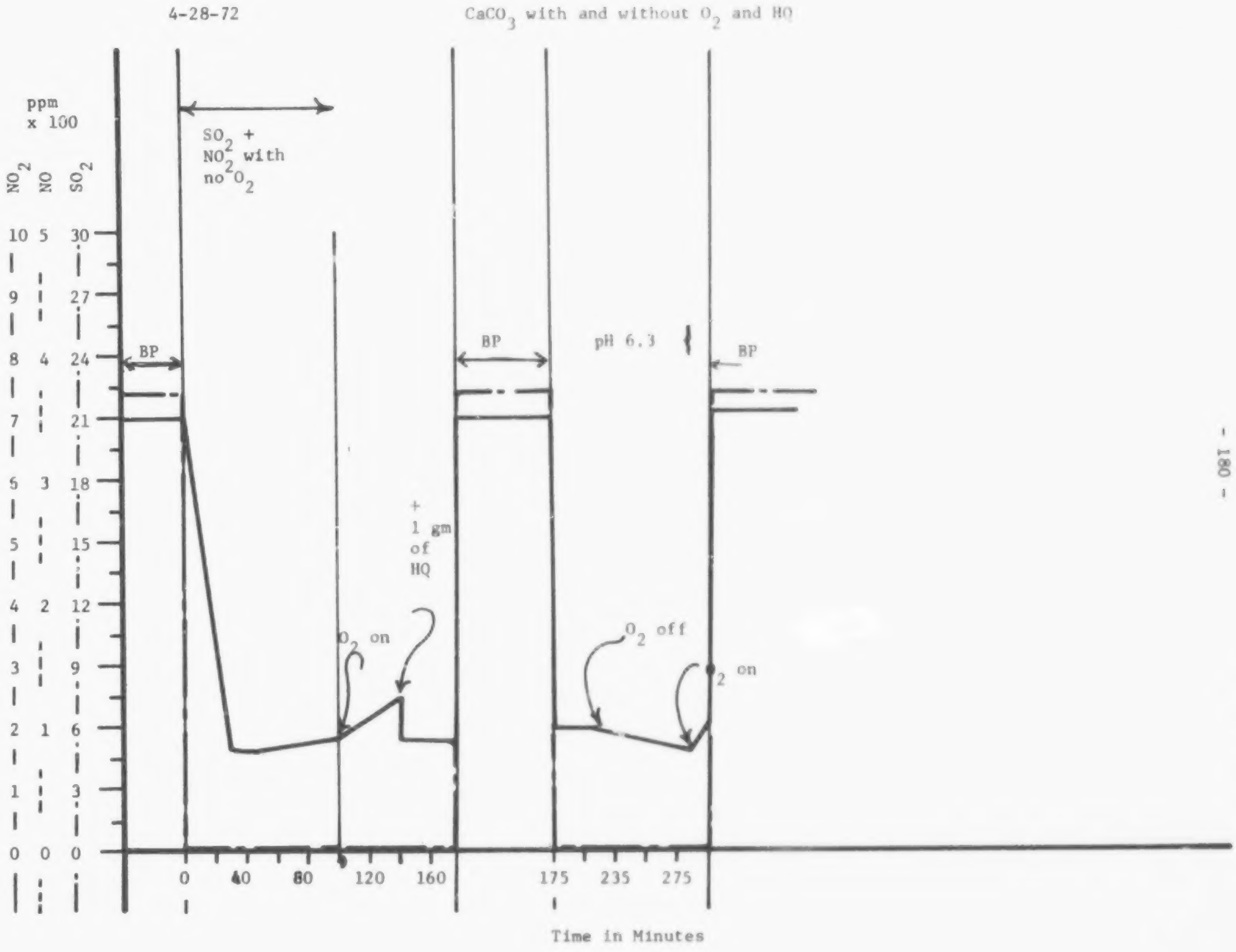
H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 700 ppm SO_2 2250 ppm

COMMENT:

(1) The increasing amounts of HQ added had greater effect and also lasted longer.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR


4-28-72
CaCO$_3$ with and without O$_2$ and HQ
ppm x 100
NO$_2$
NO
SO$_2$
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
BP
SO$_2$ + NO$_2$ with no O$_2$
O$_2$ on
+ 1 gm of HQ
BP
pH 6.3
O$_2$ off
O$_2$ on
BP
0
40
80
120
160
175
235
275
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 4-28-72

SCRUB: $CaCO_3$ slurry 10 gm in 1000 ml of H_2O (with and without HQ)

OBJECT: Absorb NO_2-SO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 124 °F	Initial pH ?*	Final pH 6.25
H_2O 10 %	CO_2 12 %	O_2 3** %
NO NA ppm	NO_2 700 ppm	SO_2 2220 ppm

COMMENT:

* pH electrodes were not working correctly (calculated pH @ 50°C = 10).

** O_2 level was varied from zero to 3%.

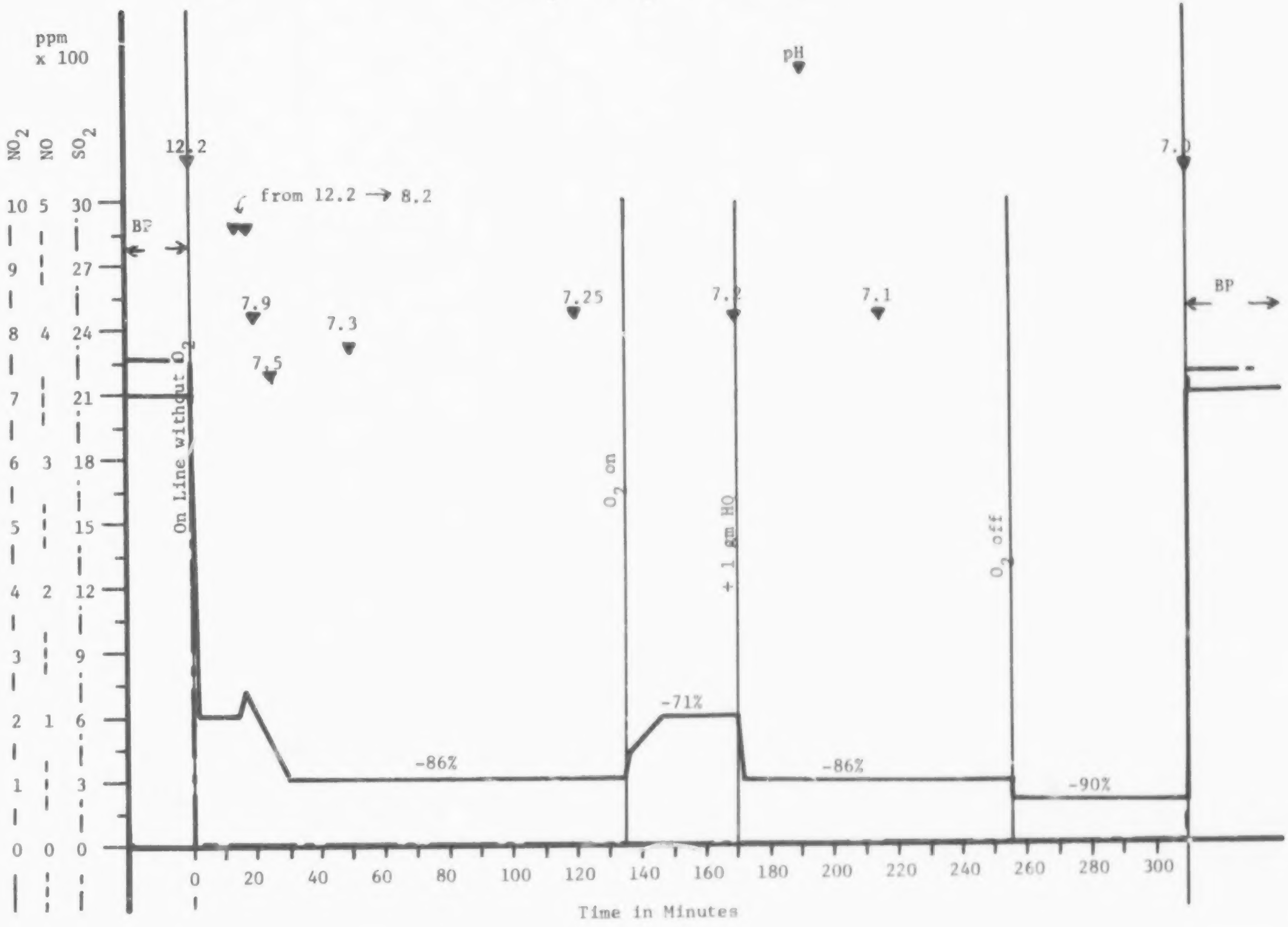
(1) NO_2 scrubbing was better without the O_2. [= 75% without and 64% with]

(2) The hydroquinone reduced the NO_2 to the O_2 free level.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR

5-1-72

Ca(OH)$_2$, Vary O$_2$ and Hydroquinone



NOX SCRUBBING DATA SHEET

DATE: 5-1-72

SCRUB: $Ca(OH)_2$ [10 gm per litre of water]

OBJECT: Vary O_2 and Hydroquinone

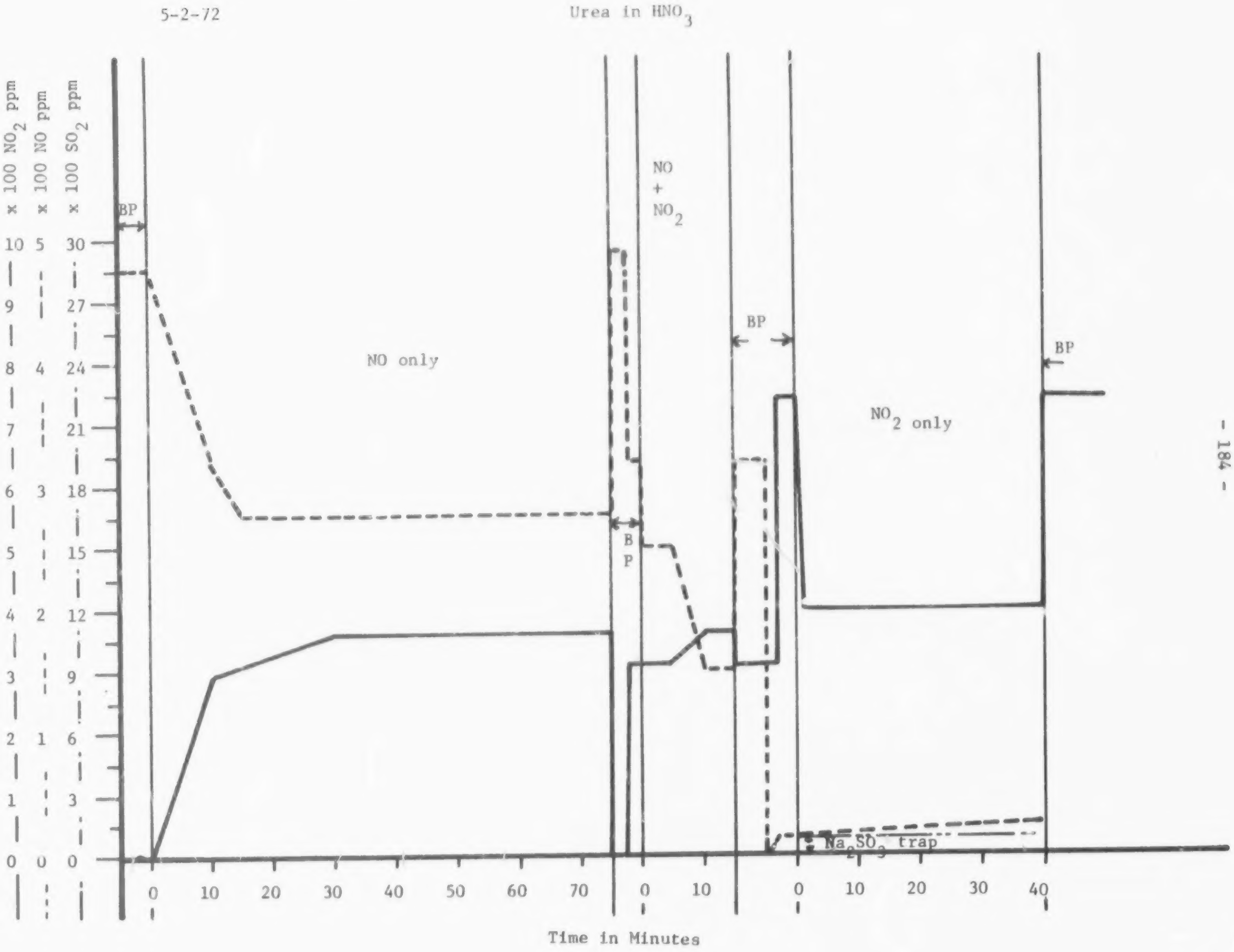
CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	123 °F	Initial pH	12.2	Final pH	7.0
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	700 ppm	SO_2	2265 ppm

COMMENT:

(1) Without O_2, absorbs approximately 86% NO_2, 100% SO_2; with O_2 = 71% NO_2 and 100% SO_2; with O_2 and HQ = 86% NO_2 and 100% SO_2.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR


5-2-72
Urea in HNO_3
x 100 NO_2 ppm
x 100 NO ppm
x 100 SO_2 ppm
10 5 30
9 27
8 4 24
7 21
6 3 18
5 15
4 2 12
3 9
2 1 6
1 3
0 0 0
BP
NO only
B
P
NO
+
NO_2
BP
NO_2 only
BP
Na_2SO_3 trap
0 10 20 30 40 50 60 70
0 10
0 10 20 30 40
Time in Minutes

NOX SCRUBBING DATA SHEET

DATE: 5-2-72 SCRUB: 28.5 gm Urea in 1000 ml 40% HNO_3

OBJECT: NO_x scrubbing with urea (NO only)

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	135 °F	Initial pH	NA	Final pH	NA
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	475 ppm	NO_2	NA ppm	SO_2	NA ppm

COMMENT:

(1) No absorption ≈ 42%.

(2) Made ≈ 360 ppm NO_2, equivalent to 75% of input NO.

(3) Frit had tendency to clog.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR

NOX SCRUBBING DATA SHEET

DATE: 5-2-72 SCRUB: Urea in HNO_3

OBJECT: NO + NO_2 Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	135 °F	Initial pH	NA	Final pH	NA
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	322 ppm	NO_2	310 ppm	SO_2	NA ppm

COMMENT:

(1) Used an open tube for 1st 5 minutes.

(2) No absorption without frit ≈ 23%; made 10 ppm NO_2.

(3) No absorption with frit ≈ 54%; made 50 ppm NO_2.

NOX SCRUBBING DATA SHEET

DATE: 5-2-72   SCRUB: Urea in HNO_3

OBJECT: NO_2 absorption

CONDITIONS: Scrub volume @ 1000 ml   Total Gas Flow @ 3200 cm^3 per minute

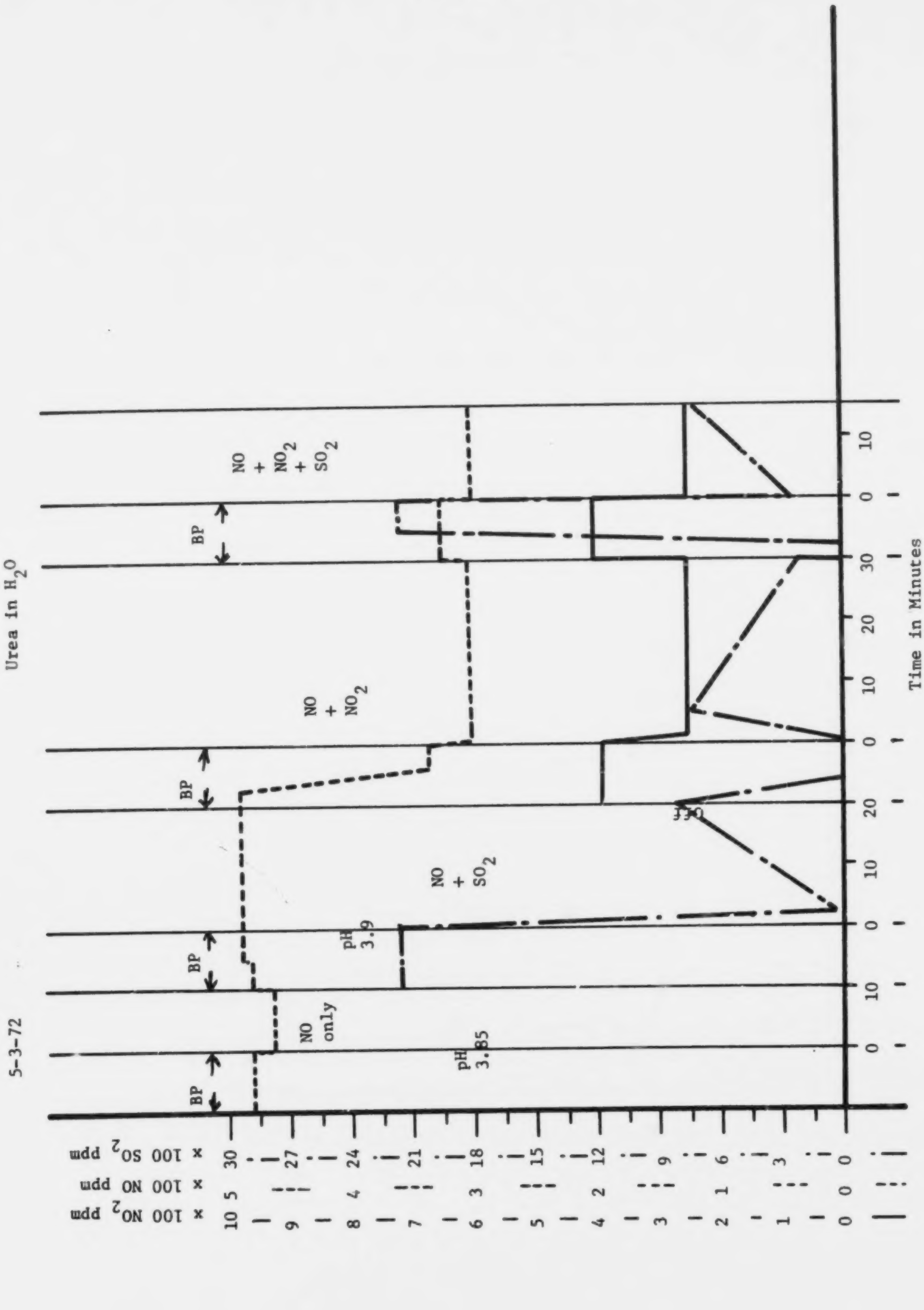
Pot Temp.	135 °F	Initial pH	NA	Final pH	NA
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	740 ppm	SO_2	NA ppm

COMMENT:

(1) Absorption of NO_2 ≈ 47%.

(2) Made ≈ 20 ppm NO.

(3) Tried adding SO_2 but frit plugged immediately.


5-3-72
Urea in H_2O
BP
NO only
NO + SO_2
NO + NO_2
NO + NO_2 + SO_2
pH 3.85
pH 3.9
Off
Time in Minutes
0
10
0
10
20
0
10
20
30
0
10
× 100 NO_2 ppm
0 1 2 3 4 5 6 7 8 9 10
× 100 NO ppm
0 1 2 3 4 5
× 100 SO_2 ppm
0 3 6 9 12 15 18 21 24 27 30

NOX SCRUBBING DATA SHEET

DATE: 5-3-72 SCRUB: Urea in H_2O [231 gm in 1 litre H_2O] 3.85 molal

OBJECT: Absorption of NO

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 3.85 Final pH 3.9

H_2O 10 % CO_2 12 % O_2 3 %

NO 480 ppm NO_2 NA ppm SO_2 NA ppm

COMMENT:

(1) About 15 ppm of NO absorbed (= 3%).

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\longrightarrow$ NDIR

NOX SCRUBBING DATA SHEET

DATE: 5-3-72 SCRUB: Urea in H_2O

OBJECT: Absorption of NO and SO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	122 °F	Initial pH	3.9	Final pH	
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	490 ppm	NO_2	NA ppm	SO_2	2154 ppm

COMMENT:

(1) Basically no absorption of NO.

(2) SO_2 level went nearly to zero and rose slowly.

NOX SCRUBBING DATA SHEET

DATE: 5-3-72 SCRUB: Urea in H_2O (solution had already been used for NO-SO_2 absorption)

OBJECT: Absorption of NO and NO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 3.9 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 339 ppm NO_2 390 ppm SO_2 NA ppm

COMMENT:

(1) NO absorption ≈ 11%.

(2) NO_2 absorption ≈ 36%.

(3) Generated 750 ppm SO_2 initially, which tappered off while running.

NOX SCRUBBING DATA SHEET

DATE: 5-3-72 SCRUB: Urea in H_2O

OBJECT: Absorption of NO, NO_2 and SO_2

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F Initial pH 3.9 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 323 ppm NO_2 400 ppm SO_2 2154 ppm

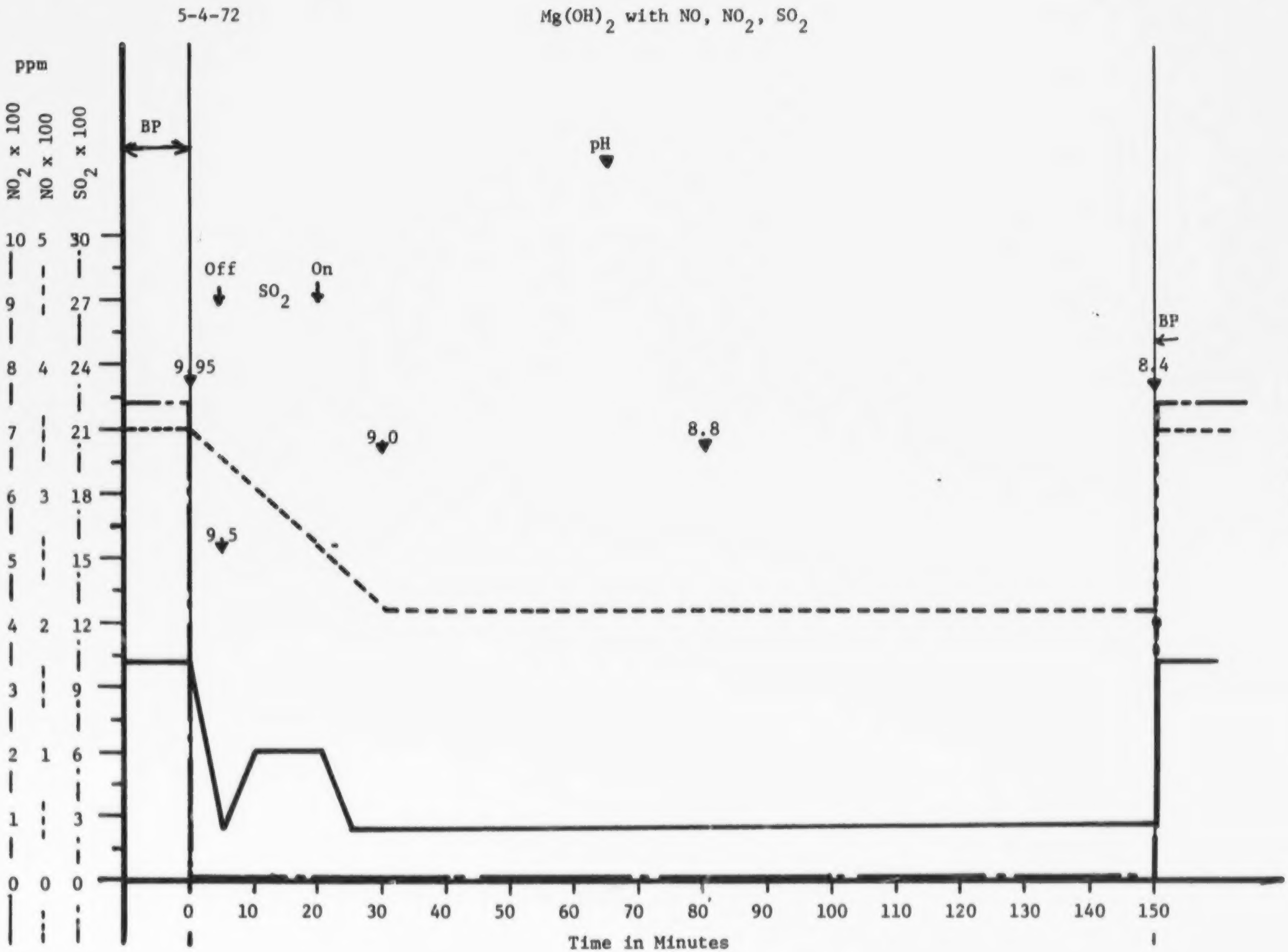
COMMENT:

(1) No absorption ≃ 7%.

(2) NO_2 absorption ≃ 38%.

(3) SO_2 absorption ≃ 89% initially; decreased with time.

Mg(OH)$_2$ with NO, NO$_2$, SO$_2$



NOX SCRUBBING DATA SHEET

DATE: 5-4-72

SCRUB: 15 gm $Mg(OH)_2$ in 1000 ml of water (slurry)

OBJECT: NO_x-SO_x Absorption

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F

Initial pH 9.95

Final pH 8.4

H_2O 10 %

CO_2 12 %

O_2 3 %

NO 350 ppm

NO_2 340 ppm

SO_2 2220 ppm

COMMENT:

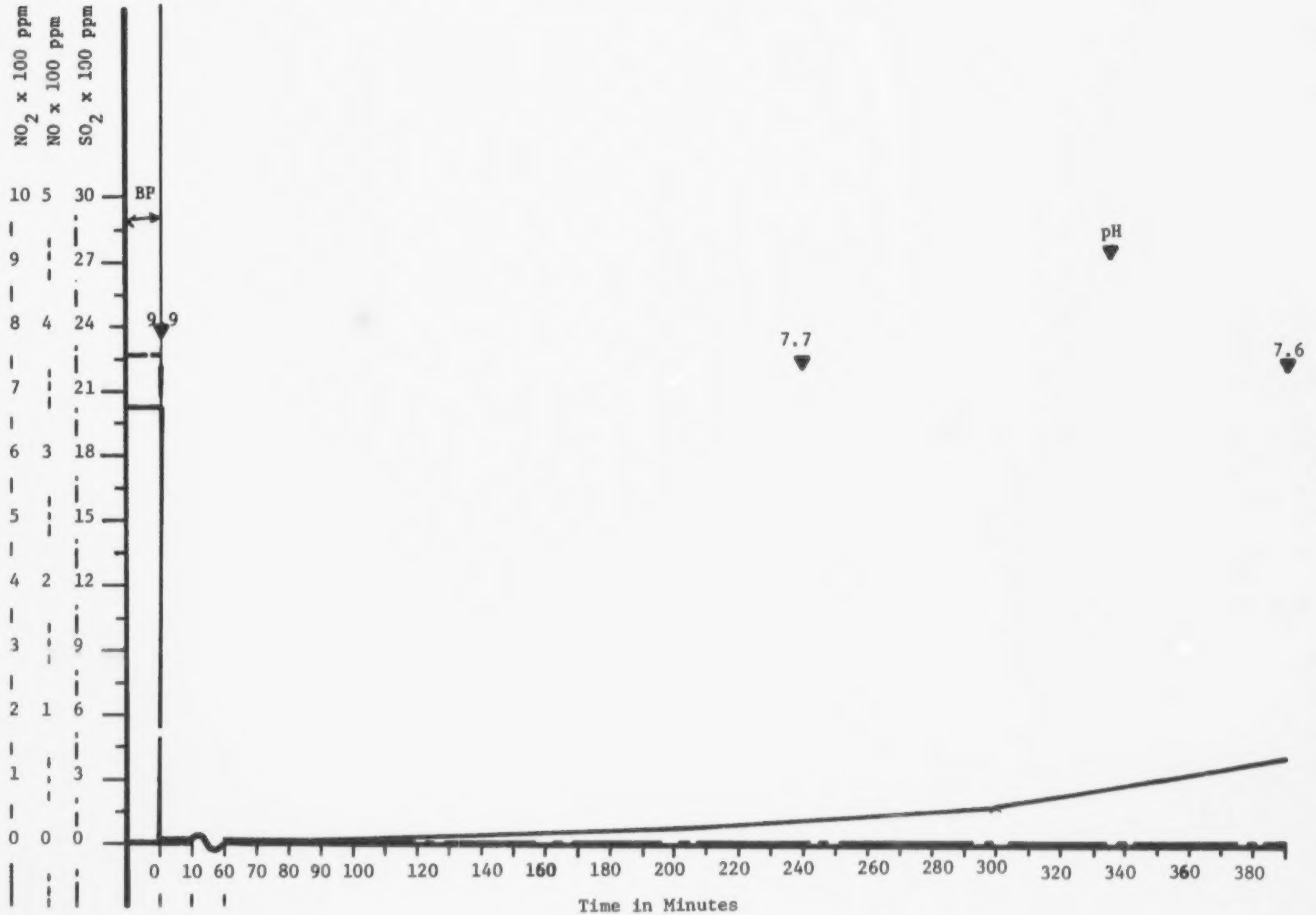
(1) More NO_2 was scrubbed then NO as would be expected (40% NO + 76% NO_2 absorbed).

(2) As usual for this type of run, all the SO_2 was scrubbed.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR

5-5-72

Mg(OH)$_2$ with Hydroquinone (Endurance Run)



NOX SCRUBBING DATA SHEET

DATE: 5-5-72 SCRUB: 15 g $Mg(OH)_2$ plus 1.0 g Hydroquinone

OBJECT: Endurance Run

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 122 °F	Initial pH 9.9	Final pH 7.6
H_2O 10 %	CO_2 12 %	O_2 3 %
NO NA ppm	NO_2 675 ppm	SO_2 2280 ppm

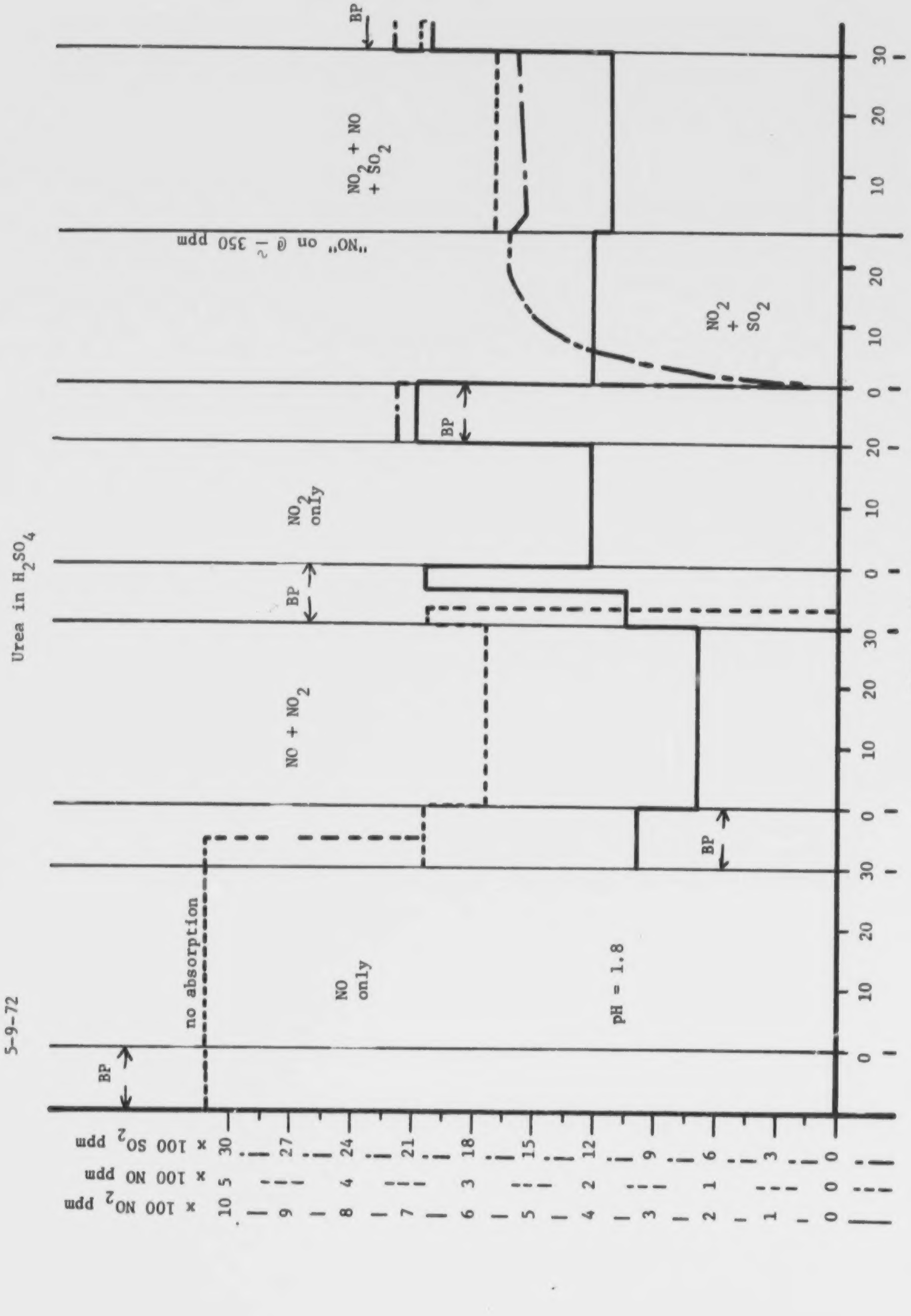
COMMENT:

(1) NO_2 dropped to zero initially; it came off zero ≈ 80 min. and rose slowly.

(2) The SO_2 dropped to zero and stayed there for the entire run.

(3) Solution became more yellow as the run progressed.

NO: Na_2SO_3 → Dry Ice → NDIR


5-9-72
Urea in H_2SO_4
BP
no absorption
NO only
pH = 1.8
BP
NO + NO_2
BP
NO_2 only
BP
"NO" on @ ≃ 350 ppm
NO_2 + SO_2
NO_2 + NO + SO_2
BP
0 10 20 30 0 10 20 30 0 10 20 0 10 20 10 20 30
Time in Minutes
× 100 SO_2 ppm
30 27 24 21 18 15 12 9 6 3 0
× 100 NO ppm
5 4 3 2 1 0
× 100 NO_2 ppm
10 9 8 7 6 5 4 3 2 1 0

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4: 1 Kg 10% urea soln + 30 ml 6N H_2SO_4

OBJECT: To absorb NO_x with urea.

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	1.8	Final pH	Not Taken
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	520 ppm	NO_2	NA ppm	SO_2	NA ppm

COMMENT:

(1) Essentially no absorption of NO.

NO: Na_2SO_3 ⟶ Dry Ice ⟶ NDIR

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 1.8 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 340 ppm NO_2 330 ppm SO_2 NA ppm

COMMENT:

(1) Some absorption of NO, ≈ 15%.

(2) Some NO_2 absorbed, ≈ 30%.

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	1.8	Final pH	
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	NA ppm	NO_2	680 ppm	SO_2	NA ppm

COMMENT:

(1) NO_2 absorption ≈ 54%.

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 1.8 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO NA ppm NO_2 700 ppm SO_2 2190 ppm

COMMENT:

(1) NO_2 absorption ≈ 40%.

(2) SO_2 absorption ≈ 21%.

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 1.8 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO ≈ 350 ppm NO_2 700 ppm SO_2 2190 ppm

COMMENT:

(1) NO_2 absorption ≈ 44%.

(2) SO_2 absorption ≈ 21%.

(3) NO absorption ≈ 18%.

NOX SCRUBBING DATA SHEET

DATE: 5-9-72 SCRUB: Urea in H_2SO_4

OBJECT:

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 125 °F Initial pH 1.4 Final pH

H_2O 10 % CO_2 12 % O_2 3 %

NO 466 ppm NO_2 NA ppm SO_2 740 ppm

COMMENT:

(1) NO absorption was zero.

(2) SO_2 absorption ≈ 10%.

(3) Information not on graph.

NOX SCRUBBING DATA SHEET

DATE: 5-15-72 SCRUB: Na_2S, 2.1 molal

OBJECT: Sulfide scrubbing, Analyze dissolved NO_x

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp.	125 °F	Initial pH	--	Final pH	--
H_2O	10 %	CO_2	12 %	O_2	3 %
NO	-- ppm	NO_2	670 ppm	SO_2	-- ppm

COMMENT:

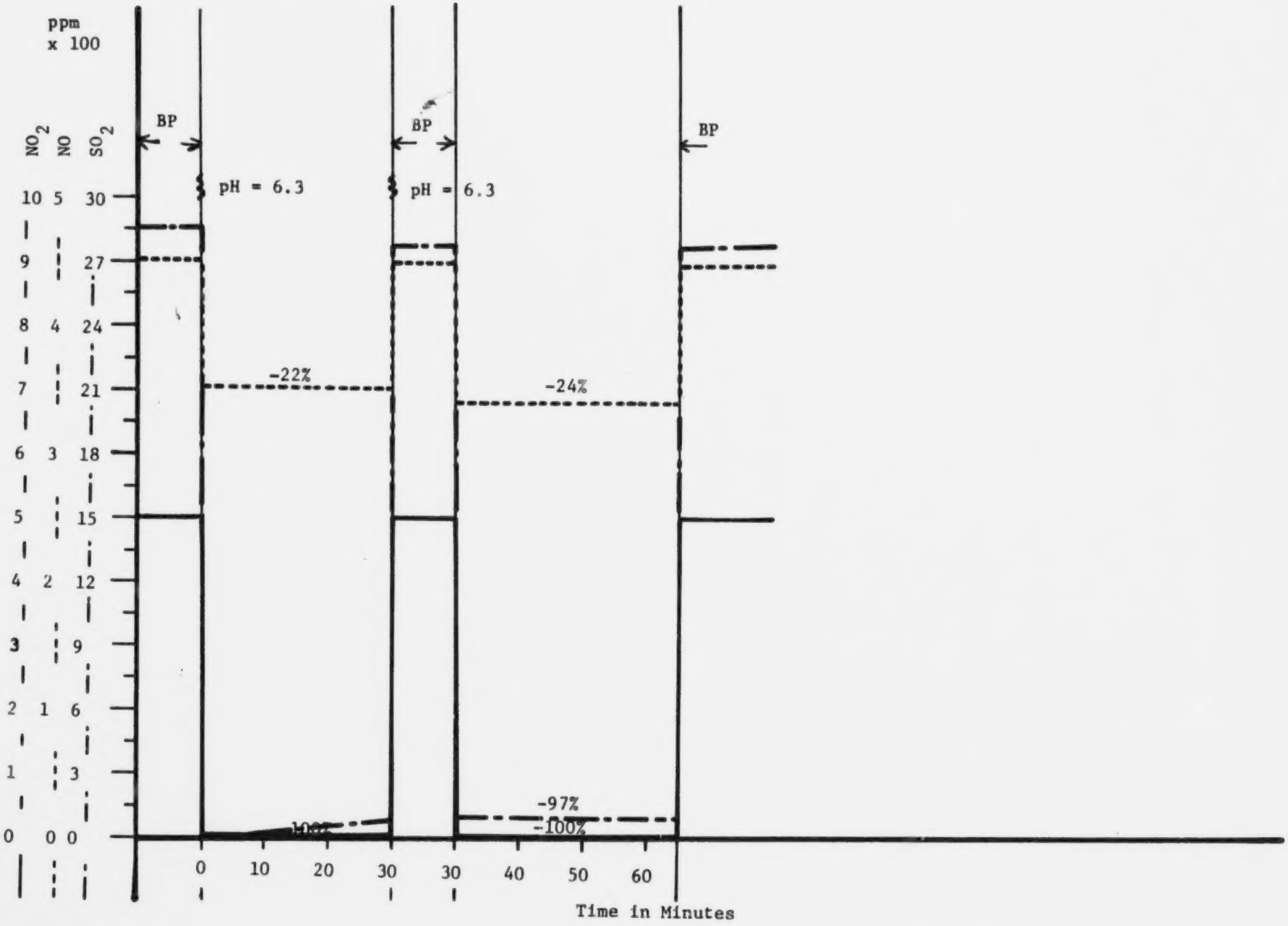
(1) ΔNO_2 = 100%, with 23 ppm NO produced.

(2) Unable to analyze solution because of spectrophotometric interference.

NO: $Na_2SO_3 \longrightarrow$ Dry Ice $\longrightarrow$ NDIR

6-22-72

$(NH_4)_2SO_3$-NH_4HSO_2 Mixture



NOX SCRUBBING DATA SHEET

DATE: 6-22-72 SCRUB: NH_4HSO_3 Mixture

OBJECT: Study Influence of Sulfate

CONDITIONS: Scrub volume @ 1000 ml Total Gas Flow @ 3200 cm^3 per minute

Pot Temp. 128 °F Initial pH 6.3 Final pH 6.3

H_2O 10 % CO_2 12 % O_2 3 %

NO 450 ppm NO_2 500 ppm SO_2 2860 ppm

COMMENT:

(1) ΔNO_2 was 100%; ΔSO_2 was 97%; and ΔNO was 24% after 1 hour.

(2) Ball sticking in the NO meter caused slight fluctuations in readings.

(3) Scrubbing solution consisted of 11.2 wt. % NH_4HSO_3, 14.6 wt. % $(NH_4)_2SO_3$, 16.6 wt. % $(NH_4)_2SO_4$, and 57.6 wt. % water. Specific gravity was 1.24.

(4) Presence of sulfate had no discernable effect.

NO: $Na_2SO_3 \rightarrow$ Dry Ice $\rightarrow$ NDIR

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